



Faculteit Bio-ingenieurswetenschappen
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CATALYTIC FAST PYROLYSIS OF BIOMASS

Güray YILDIZ

Members of the promotion committee:

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Dean, Faculty of Bioscience Engineering: Prof. Dr. ir. Guido Van Huylenbroeck
Rector, Ghent University: Prof. Dr. Anne De Paepe

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CATALYTIC FAST PYROLYSIS OF BIOMASS

DOCTORAL DISSERTATION

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Doctor (Ph.D.) of Applied Biological Sciences:
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by

Güray YILDIZ
born on April 29, 1982
in Balıkesir, Turkey

This dissertation has been approved by the promoters:

Prof. Dr. ir. Wolter Prins

Prof. Dr. ir. Frederik Ronsse

Nomenclature

Roman variables

a	TAN value of the pyrolysis oil, mg KOH/g oil
a.r.	as received feedstock basis
d.b.	on a dry feedstock basis
df	dilution factor, the ratio of added THF to produced bio-oil
L.O.I.	loss of ignition (burning the char and catalyst coke with air)
M	mass, kg
MW	molecular weight, g/mol
P	atmospheric pressure, kPa
R	universal gas constant, 8.314 L kPa mol ⁻¹ K ⁻¹
s	seconds
T	temperature, °C
T_g	product gas temperature, K
t_{run}	experimental run time, min.
U	superficial gas velocity, m/s
U_{mf}	minimum fluidization velocity, m/s
vol. %	volume percentage
vol% _i	volume percentage of non-condensable gas component i, μ -GC readout
vol% _{total}	total volume percentage of detectable non-condensable gases, μ -GC readout
w	water content of the pyrolysis oil, g of water/g of liquid
WHSV	weight hourly space velocity, h ⁻¹
wt. %	weight percentage, g/g
X	yield of a non-condensable gas compound, wt. % on feed (a.r.)
Y	yield, wt. % on feed (a.r.)

Greek symbols

$\Phi_{g,avg}$	average gas flow rate, L/h
Φ_{N_2}	inert gas flow rate, L/h
Φ_{pine}	flow rate of pine wood, g/h
τ	residence time, s

Subscripts

i	a single component in a group of components
<i>feed</i>	biomass fed to the system during a run
<i>liquid</i>	the liquid produced during a run
<i>organic liquid</i>	the organic fraction of produced liquid during a run
<i>water</i>	the water fraction of produced liquid during a run

<i>gas</i>	the gas produced during a run
<i>char</i>	the char produced during a run
<i>system carbon</i>	the system carbon produced during a run
<i>solid mix</i>	the mixture of heat carrier + char after sieving
<i>char in mix</i>	char in the mixture of heat carrier + char
<i>liq.mix.</i>	produced liquid + added THF
<i>THF in liq.mix.</i>	THF in the liquid mixture
<i>hc</i>	heat carrier
<i>hc,i</i>	initial (amount of) heat carrier that is loaded to the heat carrier hopper
<i>hc,f</i>	final (amount of) heat carrier that is loaded to the heat carrier hopper
<i>ex situ cb, i</i>	initial ex situ catalyst blend
<i>ex situ cb, f</i>	final ex situ catalyst blend
<i>moisture, hc</i>	moisture of heat carrier
<i>kvs</i>	collected solids in the knock-out vessel
<i>cs</i>	collected solids in cyclone
<i>sc</i>	spent catalyst
<i>filtrate</i>	filtered solids out of pyrolysis oil
<i>hc, coke</i>	coke in the heat carrier
<i>kvs, coke</i>	coke in the collected knock-out vessel solids
<i>cs, coke</i>	coke in the collected cyclone solids
<i>sc, coke</i>	coke in the spent catalyst sample
<i>filtrate, coke</i>	coke in the filtered solid out of pyrolysis oil
σ	standard deviation
<i>pine</i>	biomass feedstock used
<i>bed material</i>	sand or sand-catalyst mixture introduced to the reactor
<i>vapours</i>	generated pyrolysis vapours
<i>bio-oil</i>	liquid product (including generated water)
<i>ESP,out</i>	electrostatic precipitator subsequent to the experiment
<i>ESP,in</i>	electrostatic precipitator prior to the experiment
<i>gc,out</i>	glass spiral condenser subsequent to the experiment
<i>gc,in</i>	glass spiral condenser prior to the experiment
<i>cf,out</i>	cotton filter subsequent to the experiment
<i>cf,in</i>	cotton filter prior to the experiment
<i>fs</i>	filtrate solids
<i>solids,i</i>	carbonaceous solids (sum of char, heterogeneous coke, and system deposits), before L.O.I. (loss on ignition)
<i>solids,f</i>	carbonaceous solids (sum of char, heterogeneous coke, and system deposits), after L.O.I. (loss on ignition)

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Abstract

Utilization of biomass offers a potential to sustain the current petro-chemical economy for the production of chemicals and (transportation) fuels on basis of renewable resources. Crude bio-oil derived from fast pyrolysis of lignocellulosic biomass is a mixture of water (15–30 wt.%) and various oxygen containing organic compounds. The presence of oxygen in bio-oils (*ca.* 35–40 wt.%) is commonly believed to be the origin of problems caused by its high water content (15–30 %), corrosiveness (pH of 2–3), relatively low heating value compared to fossil fuels (*ca.* 17 MJ/kg), poor volatility, and high viscosity (35–1000 cP at 40 °C). However, not only the level of oxygen in the bio-oil is too high, but also the way it exists (functionality) is a part of the problem. Improving the quality of the bio-oils, whether or not in combination with a certain degree of oxygen removal, would include a selective transformation of certain oxygen functionalities such as acids and aldehydes into ‘desired’ or acceptable ones like alcohols, phenols, and ethers. Application of heterogeneous catalysis in fast pyrolysis (*i.e.* catalytic fast pyrolysis; CFP) may lead to a liquid product (*i.e.* catalytic fast pyrolysis oil, CFP-oil) with an improved quality compared to that of crude bio-oil. Here, the improvement in bio-oil quality refers to the production of either high yields of transportation fuel compounds (*e.g.* aromatics, olefins) and specialty chemicals (*e.g.* phenolics), or just a drop-in refinery feedstock to be blended with the feed streams of existing petroleum refineries. While the literature on catalytic fast pyrolysis of biomass –mainly focussed on catalyst screening– is rapidly expanding, there is an urgent need for the translation of laboratory results to viable process concepts and bench/pilot plant trials. Together with the development of efficient catalysts, the design and the intensification of the process with efficient heat integration are of significant importance in the catalytic conversion of lignocellulosic biomass to the targeted liquid product. The present thesis discusses the catalytic fast pyrolysis of lignocellulosic biomass in a process oriented way that may initiate a useful process technology development in the near future. The final goal is to come up with recommendations and suggestions on how to realize this technique at a commercial/industrial scale. That requires a better understanding of the precise effects of the essential process parameters (*e.g.* processing mode; in- or ex situ) and design elements (*e.g.* reactor type, catalyst type) on the one hand, and definitions and outcomes of possible obstacles (*e.g.* successive regeneration of the catalyst, effect of biomass ash) on the other.

In this work, two types of continuously operated (catalytic) fast pyrolysis reactors were used, *viz.* an auger reactor and a mechanically stirred bed reactor. In all experiments performed in both setups, pine wood with a particle size range of 1 to 2 mm was pyrolyzed at a constant reactor temperature of 500 °C. In the auger reactor, first the effect of the operation mode on the product yields and compositions has been investigated while using a single type of heterogeneous ZSM-5 based acidic catalyst. Two operation modes were tested. In situ operation includes the mixing of biomass and catalyst inside a single reactor, while ex situ refers to catalytic treatment of the pyrolysis vapours in a secondary reactor. A second study

was concerned with the screening of various heterogeneous catalysts (and their metal doped counterparts) in in situ operation. In all experiments, the presence of catalysts led to the production of additional water, coke and gases at the expense of the liquid organics and char. The overall performance of in situ catalysis in terms of oil quality was considerably better than that of ex situ catalysis; more aromatics and phenols were produced in the case of in situ operation. That may be caused by different vapour residence times and vapour-catalyst contact times. Among all eight catalysts tested, the acidic catalyst containing some redox active metal, the basic catalyst with a mixture of two metal oxides (calcined), and a metal oxide doped gamma-alumina catalyst (calcined) were found to be the best performing ones, based on both the deoxygenation requirements and the production of desirable compounds in high yields.

In the mechanically stirred bed reactor, we studied *i)* the effect of a repeated catalyst regeneration (eight cycles in total), and *ii)* the effects of the pine wood ash on the yields and composition of the products. In all catalytic experiments, a single type of a ZSM-5 based catalyst was used in situ. Along the reaction/regeneration cycles, trends in pyrolysis product yields converging to that of non-catalytic levels were observed. This revealed that the activity, and thus the influence of the catalyst slowly declined, which was confirmed by a BET surface area reduction of 63 %. Ash concentrations as low as *ca.* 3 wt.% relative to the amount of pine wood fed, and *ca.* 0.002 wt.% relative to the amount of bed material, were found sufficient to affect the yield and composition of the CFP products unfavourably.

Finally, the technical and operational barriers for the implementation of catalytic fast pyrolysis technology are discussed while focusing on the process modes and parameters, economical use of the primary and secondary products, and heat integration. Some process alternatives for an efficient CFP operation are suggested as well.

Research has, until now, been focused mainly on screening and small-scale testing of various catalysts. One challenge in developing CFP of biomass is the design and large scale production of such catalysts to enable testing in continuously operated, bench and pilot scale installations. FCC type of catalysts are the only suitable ones commercially available. But they are developed especially for use in a riser reactor and short contact times (differing significantly from typical biomass devolatilization times). The main problem in CFP of biomass was found to be the presence of the biomass originated alkaline ash which eventually poisons any catalyst in case of direct contact. In a commercial process, a solution may be to separate the biomass fast pyrolysis from the catalytic treatment of the vapours (*i.e.* ex situ processing mode) where the physical contact between the biomass minerals and the catalyst is excluded. Even though this requires significant process adjustments, ex-situ processing allows the catalyst to be re-used in a much larger number of reaction/regeneration cycles than in case of in situ operation.

Abstract

Het gebruik van biomassa biedt het potentieel om de huidige petrochemie-gebaseerde economie te ondersteunen met hernieuwbare grondstoffen voor de productie van chemicaliën en transportbrandstoffen. Ruwe bio-olie, geproduceerd door snelle pyrolyse van lignocellulose biomassa, is een mengsel van water (15–30 gew.%) en tal van zuurstof bevattende organische verbindingen. De aanwezigheid van zuurstof in bio-olie (ong. 35–40 gew.%) wordt algemeen aangenomen de oorzaak te zijn van verschillende problemen in de toepassing ervan, zoals hoog watergehalte (15–30 gew.%), corrosiviteit (pH 2 tot 3), redelijk lage stookwaarde (ong. 17 MJ/Kg) in vergelijking met fossiele brandstoffen, lage vluchtigheid en hoge viscositeit (35 tot 1000 cP bij 40 °C). Echter, niet alleen de concentratie aan zuurstof in bio-olie is te hoog, ook de manier waarop deze zuurstof gebonden is, ligt aan de basis van de aangehaalde problemen. Het verbeteren van de kwaliteit van bio-oliën, al dan niet in combinatie met een zekere graad van zuurstofverwijdering, zou een selectieve transformatie van zekere, ongewenste zuurstof-functionaliteiten (zoals zuren en aldehyde) in ‘gewenste’ (zoals alcoholen, fenolen en ethers) moeten inhouden. De toepassing van heterogene katalyse in snelle pyrolyse (katalytische snelle pyrolyse) kan leiden tot een vloeibaar product met verbeterde eigenschappen in vergelijking met klassieke, ruwe bio-olie. Het verbeteren van de kwaliteit van de bio-olie verwijst hier naar ofwel de productie van transportbrandstoffen (alifaten en aromaten) en fijnchemicaliën en dit in hoge opbrengsten, ofwel naar de productie van een voeding dewelke kan worden gemengd met bestaande voedingen in de klassieke petrochemische raffinaderij. De literatuur inzake snelle katalytische pyrolyse, voornamelijk inzake de screening van nieuwe katalysatoren, breidt snel uit. Echter, er is een noodzaak aan de vertaling van de resultaten behaald op laboschaal naar piloot en volle schaal systemen. Tezamen met de ontwikkeling van efficiënte katalysatoren, het ontwerp en de intensificatie van het proces, alsook de efficiënte benutting van restwarmte zijn belangrijke aandachtspunten in de ontwikkeling van katalytische snelle pyrolysesystemen voor de productie van het gewenste vloeibaar product. Dit doctoraal proefschrift behandelt de snelle katalytische pyrolyse van lignocellulosehoudende biomassa vanuit een procesmatige zienswijze met de bedoeling om nuttige technologie-ontwikkeling te ondersteunen in de nabije toekomst. Het ultieme doel is het formuleren van aanbevelingen en suggesties om deze technologie toe te passen op commerciële en industriële schaal. Dit noodzaakt enerzijds een beter begrip van de effecten van procesparameters (verwerkingsmodus; in-situ of ex-situ) en het ontwerp (reactor, katalysator), en anderzijds de identificatie van potentiële problemen (v.b. herhaaldelijk regenereren van de katalysator; het effect van as in de biomassa) alsook de eruit voortvloeiende gevolgen.

In dit experimenteel onderzoek werden twee continue snelle pyrolysereactoren gebruikt, met name een schroefreactor en een geroerde bed reactor. Voor alle uitgevoerde experimenten werd dennenhout vermalen tot een deeltjesgrootte van 1 tot 2 mm, gebruikt en werd deze steeds gepyrolyseerd op een temperatuur van 500 °C. Eerst werd het effect van katalyse-

modus op de opbrengst en samenstelling van de gevormde producten, bestudeerd aan de hand van de schroefreactor en dit met één enkel type van ZSM-5 gebaseerde zure katalysator. Twee katalyse-modi werden getest: In-situ modus houdt in dat de biomassa en de katalysator in de reactor samen worden gemengde, terwijl in de ex-situ modus enkel de pyrolysedampen in contact worden gebracht met een katalysator, en dit in een aparte reactor. Vervolgens richtte een tweede studie zich op het screenen van verschillende heterogene katalysatoren in de in-situ modus. In alle experimenten werd er vastgesteld dat de aanwezigheid van de katalysator aanleiding gaf tot een meerproductie van water, coke en permanente gassen en dit ten koste van het vloeibaar product en kool. De algehele performantie van in-situ katalysatoren, en dit op basis van bio-olie kwaliteit, was aanzienlijk beter dan deze van ex-situ katalyse. Er werden meer fenolen en aromaten gevormd bij de in-situ katalysemodus. Deze waarneming kan verklaard worden aan de hand van verschillen in dampverblijftijden en damp-katalysator contacttijden. Er werden acht katalysatoren getest, waarvan de types behoorden tot een zure katalysator gedopeerd met een specifiek redox metaal, een basische katalysator met een mengsel van twee metaaloxiden en een metaaloxide katalysator aangebracht op gamma-alumina. Uit deze reeks werd de metaaloxide op alumina bevonden als de best presterende, en dit op basis van zuurstofverwijdering en de vorming van gewenste componenten in de bio-olie als criteria.

In de reactor op basis van een geroerd bed, werden achtereenvolgens bestudeerd: (1) het effect van herhaaldelijke regeneratie van de katalysator (8 cycli in totaal) en (2) het effect van de accumuleren biomassa-as op de opbrengst en samenstelling van het vloeibaar product. Telkens werden de experimenten uitgevoerd met één enkel type van ZSM-5 gebaseerde katalysator en dit in de in-situ katalysemodus. Naarmate de katalysator verschillende regeneratiecycli had doorlopen werd vastgesteld dat de opbrengst van de pyrolyseproducten convergeerde naar deze van een niet-gekatalyseerd pyrolyseproces. Deze waarneming duidt aan dat de activiteit van de katalysator gestaag verminderde, wat ook worden vastgesteld door een vermindering van het specifiek oppervlak van de katalysator met 63%. Lage concentraties van as, ongeveer minder dan 3 gew.% (op basis van hoeveelheid gevoede biomassa) en ongeveer 0.002 gew.% (op basis van massa aan bedmateriaal), werden voldoende actief bevonden om de opbrengst en de samenstelling van de bio-olie negatief te beïnvloeden.

Tenslotte beëindigd deze scriptie met een uiteenzetting van en een discussie over de implementatie van de katalytische snelle pyrolyse-technologie. Aandacht werd besteed aan de proces-modi, procesparameters, het economisch rendabel gebruik van primaire en secundaire pyrolyseproducten en het hergebruik van restwarmte. Verschillende alternatieven voor efficiënte bedrijving van snelle katalytische pyrolyse werden tevens besproken.

Het onderzoek binnen het domein van katalytische snelle pyrolyse heeft zich tot op heden voornamelijk gericht op het uitvoeren van kleinschalige of microreactor experimenten. Een blijvende uitdaging binnen dit veld is de opschaling van de productie van geschikte katalysatoren om deze te kunnen testen in continue piloot en volle schaal installaties. Tot op heden zijn enkel FCC-type katalysatoren de enige die in dergelijke hoeveelheden commercieel beschikbaar zijn. Echter deze uit de petrochemie afkomstige katalysatoren zijn specifiek ontworpen voor het gebruik in riser reactor en dit met overeenkomstige, korte contacttijden (en dewelke aanzienlijk verschillen van de tijden benodigd om biomassa te

vervluchten in pyrolyse). Het hoofprobleem in katalytische snelle pyrolyse werd geïdentificeerd als zijnde de aanwezigheid van de as, afkomstig van de biomassa en rijk aan alkalimetalen. Deze as komt in contact met de katalysator en kan deze vervolgens deactiveren. Een oplossing in een commercieel proces kan bestaan uit de scheiding van het pyrolyseproces en de katalyse, met name door enkel de dampen in contact te brengen met een katalysator (ex situ katalysemodus). Hierdoor wordt rechtstreeks contact tussen de katalysatoren en de van biomassa afkomstige as, vermeden. Hoewel dit ingrijpende wijzigingen in de procesuitvoering noodzaakt, zou het toepassen van ex-situ katalyse een aanzienlijk groter aantal regeneratiecycli toelaten in vergelijking met een proces bedreven volgens de in-situ katalysemodus.

Chapter 1

General introduction

In this introduction, the general overview on world energy supply is given, followed by a discussion regarding the (potential) role of biomass as a source for energy and fuels. Then, a brief introduction into catalytic fast pyrolysis of biomass, a thermochemical process for biomass conversion aiming to produce energy, (transportation) fuels, and chemicals, is provided. Finally, the outline of the following chapters is given.

1.1 General overview on world energy supply

The world's total energy supply doubled over the last 40 years, and reached 13,371 MToe (million tonnes of oil equivalent) by 2012 [1]. Of this supply, 81.7 % of the total energy is provided by fossil fuels, while nuclear and renewable energy sources provide 4.8 % and 13.5 % of the total energy supply, respectively [1]. The growing need for energy can for a large part be ascribed to the projected growth of the world population with 40 % in 2050 and the related increase in the energy consumption of 47–66 % between 2010 and 2050 [2]. The energy policies that are largely based on the use of fossil fuel resources have many adverse bottom lines and aftereffects. In the past decades, the awareness of risks and harmful consequences resulting from the intensive use of fossil fuels like coal (including peat and oil shale), crude oil, and natural gas has increased. The main concerns are [3]:

- dependency on fossil fuel supplying countries in politically unstable regions [4],
- insecurity of supply by a lack of diversification in energy resources,
- technical risks, such as oil rig explosions in open sea (*e.g.* BP Deepwater Horizon disaster in 2010), coal mine collapses, *etc.*,
- increasing carbon dioxide (CO₂) emissions, an important perpetrator of global warming,
- depletion of fossil fuel resources within a limited time period; the proven oil, natural gas, and coal reserves are expected to last for 53, 55, and 113 years, respectively [5],
- gradually rising energy prices due to dwindling fossil resources; this forces industry to diversify their energy input from a purely economic point of view.

By 2012, 68 % of the world's total generated electricity is from fossil resources [1]. Without the emission of greenhouse gases, the electricity can, indeed, be generated by nuclear energy, as well. The share of nuclear energy in electricity production was calculated to be 11 %, by 2012. However, the world's present measured resources of uranium (used in nuclear reactors) are projected to last for 90 years [6] and there is an ongoing debate regarding the use of nuclear energy. The rising concerns regarding the disposal of nuclear wastes and possible nuclear disasters/radioactive incidents led to a review of nuclear energy usage worldwide. The recent catastrophe in Fukushima-Japan on 11 March 2011 showed that a nuclear power plant accident can have drastic consequences for the environment. Recently, Germany has decided to shut down 17 nuclear reactors permanently, which fuel 18 % of the country's power needs. Under Germany's Atomic Energy Act, the last nuclear power plant will be put out of service by 2022 [7,8].

These direct and indirect adverse consequences related with the use of fossil resources and potential risks linked with the nuclear energy stimulate countries to develop local alternative energy programs from unconventional sources. This leads the determination of future energy strategies based on the development of renewable energy technologies. These include wind, tidal, solar, wave, hydro, geothermal, and biomass [3]. The production of energy (in the form of electricity) is possible with all these renewable sources. However, next to the energy production, the production of industrially important petrochemical end-products such as transportation fuels, polymers, specialty chemicals, *etc.* is important, as well. This is

exclusively possible with the use of biomass because it is the only renewable resource of carbon. Hence, the development of renewable energy technologies including the utilization of biomass is crucial for global sustainability.

1.2 Biomass as a source for energy and fuels

The supply of renewable energy is one of the main challenges that mankind will face over the coming decades. In that respect, biomass can offer a renewable and sustainable source of raw materials that can either lead to the production of biofuels and/or biochemicals. The current usage of biomass-derived fuels together with waste accounts for 12.4 % of the total energy consumed in the world [1], but most of it is directly combusted in developing countries to locally provide heat (cooking stoves) and power. The bio-energy production chain is relatively labour-intensive and may provide many skilled and unskilled local jobs, also in developing countries. If carefully managed, biomass-derived energy could provide several improvements in energy security and trade balances, by substituting imported fossil fuels (at least partially) with domestic biomass. The European Commission and various public and private organizations believe that biomass, for the production of fuels and chemicals, will play a crucial role in meeting Europe's "2020" targets. That is said, by the year 2020, renewable energy sources should represent 20 % of Europe's final energy consumption, greenhouse gas emissions should be reduced by 20 %, and energy efficiency should increase by 20 %, compared to 1990 levels [9]. Recently (on 22 January 2014), the European Commission put forward the 2030 energy and climate targets of a 40 % reduction in greenhouse gas emissions (compared to 1990) and a share of 27 % renewables in final energy consumption [10]. Moreover, the energy scenario of Shell predicts an increase of 2.5 to 3 times the current biomass usage in 2050 [2].

Recently, power to gas plants, based on the production of hydrogen via electrolysis has gained interest [11]. The generated hydrogen can be directly fed into the existing natural gas grid, stored in caverns or tanks, used as fuel for hydrogen vehicles, converted back into electricity, or used in the chemical industry to produce *e.g.* ammonia. Alternatively, in a further process step, the generated hydrogen can be converted into methane through the addition of carbon dioxide, using the Sabatier process. Eventually, this process relies on the CO₂ which is mainly produced from biomass materials in the biogas plants. Hence, among the various sustainable energy options (solar, wind, geothermal, *etc.*), biomass is the only renewable energy resource that consists of actual matter (predominantly C, H, O, and N) [12]; this makes it suitable for the production of carbon-based fuels, fuel intermediates, and chemicals. Biomass derived from agricultural and forestry waste (consisting mainly of lignocellulose) is typically produced in quantities of around 10 tons dry material per hectare annum [13,14] depending on various factors (*e.g.* soil quality, climate). Biomass grown especially for energy production (miscanthus, poplar, willow, *etc.*) can have higher yields, *viz.* up to 20 tons/ha. The highest potential is in the utilization of waste and residues, which are cheap and do not pose the problem of land use change (*i.e.* soil used for food production is converted to soil for bio-energy production).

Biofuels, produced from purposely grown energy crops (*e.g.* sugar-, starch-, or lipid-rich plant material), are called first generation biofuels. These are based on the utilization of biomass feedstock that can also be used in the food chain. The sugars and vegetable oils in this biomass feedstock can be converted into bio-ethanol and bio-diesel (from rapeseed, sunflowers, *etc.*), respectively. By 2013, worldwide total biofuels production was calculated to be 65.3 million tonnes oil equivalent, with an increase of 9.7 % compared to 2010 [5]. However, the scale of production of these first generation biofuels currently appears to be several orders of magnitude lower than typical unit operations in conventional oil refineries (100 MW compared to several GW's in oil refineries). The second type of biofuels is produced from the conversion of lignocellulosic biomass and various wood-based residues (forestry, agricultural, and industrial residue) [3] and are known as second generation biofuels. Because of the concerns about the competition with food production for the first generation biofuels based on sugar, starch, and vegetable oils, the interest in biofuels has now been shifted towards the second generation biofuels from (non-edible) biomass resources. Moreover, the availability of biomass for the production of first generation biofuels is very limited (<10 EJ/yr); while for second generation biofuels it is significant (*ca.* 100 EJ/yr) [15]. It is expected that the air and sea transportation sectors will be particularly heavy users of second generation biofuels [16]. The term third generation biofuels has recently entered the mainstream; it refers to biofuels derived from algae. Third generation biofuels are considered to be a viable alternative energy resource that has a very short harvesting cycle (*ca.* 1–10 days depending on the process) and higher oil production efficiency (15–300 times) than traditional crops on an area basis [17].

1.3 Conversion of biomass to energy, fuels, and chemicals

In recent decades, the need to meet the increasing energy demands, without damaging the environment and sacrificing the world's resources too quickly, gave an important impetus to the development of technologies for biomass conversion to modern energy carriers such as electricity, liquid biofuels, syngas, hydrogen, and methane. Biomass alone is, indeed, not able to solve the world's energy needs but can contribute to the energy production. It can partially satisfy the need for the synthesis of carbon containing raw materials, as well [18]. The unique composition of biomass makes it especially suitable for the production of value-added chemicals and materials that can replace petrochemicals [19,20]. However, the practical examples are limited at this stage due to the difficulties in the isolation of individual chemical compounds from bio-oils. The production of such chemicals from lignocellulosic biomass could enhance the economic viability of a society whose needs for energy and materials depend on renewables.

Significant efforts are made in using biochemicals for the replacement of traditional fossil sources used in industry for non-energy purposes, such as in the production of bulk-, intermediate-, fine- or specialty chemicals, pharmaceuticals and organic materials. Currently, the total energy content in all oil and oil products consumed as feedstock in the petrochemical industry amounts to 800 TWh in the European Union and 4,300 TWh worldwide [9]. The utilization of biomass with suitable and efficient conversion technologies can, in principle,

contribute to this supply-demand chain, and thus partially decrease the dependency on fossil fuel resources.

Although bio-based products are generally more environmentally friendly than those derived from petroleum based feedstocks, they are considerably more expensive to produce, due to the lack of practical and efficient process methodologies. Thus the huge potential lying in renewable feedstocks is largely untapped. Biomass conversion to an intermediate, liquid energy carrier and source of chemicals, at a scale that matches the local logistics of collection and storage, seems attractive in case it [21]:

- has an energy density of up to 10 times (on a volume basis) higher than the original biomass material; this greatly facilitates biomass logistics,
- can be stored and handled easily as a uniform low-viscosity liquid without any risk of natural degradation,
- can be collected from various production areas and shipped easily over long distances to central sites for further processing,
- can be pressurized and pumped through pipelines,
- can be used as a source of oxygenated and deoxygenated chemicals,
- can be co-fed to a conventional crude oil refinery.

Such a conversion process should preferably:

- be safe, simple, and easy to operate at moderate temperatures,
- produce a stable non-toxic uniform liquid, with a high energy density and favourable storage, transport, and combustion properties. The liquid product is preferred to include the possible maximum amount of targeted specialty chemicals (*e.g.* aromatics, phenols),
- have a high liquid yield and high thermal efficiency,
- have favourable economics even at low production capacities (10,000–50,000 ton/year)
- be feedstock-flexible, accepting all kinds of biomass and residues,
- recover the minerals embedded in the biomass feedstock and allow them to be returned to the soil as essential nutrients belonging to the production area.

A biomass conversion process fulfilling all the above mentioned criteria is not (yet) available. In principal, there are three types of biomass conversion processes: biological (*e.g.* ethanol production by fermentation), mechanical/physical (*e.g.* oil extraction from seeds), and thermo-chemical processes [3]. The latter include direct combustion, gasification, hydrothermal gasification, hydrothermal liquefaction (HTL), torrefaction, slow pyrolysis, and fast pyrolysis. Among these technologies for the conversion of biomass to liquid, solid and gaseous fuels, HTL and fast pyrolysis are considered as promising technologies for the conversion of biomass to high energy density liquids (bio-oil) at high yields and, hence, are the most suitable to fulfil the high future demands for biofuels and biochemicals. However, in terms of process economics, fast pyrolysis seems more advantageous than HTL since the latter is performed under high pressures (7 to 30 MPa) [22]. Besides, HTL is particularly

attractive for the processing of wet biomass feedstocks, in which feedstock drying prior to the pyrolysis process would consume too much energy.

To decrease the dependency of crude oil for the production of fuels and chemicals, the – partial– replacement of crude oil with biomass as raw material is an interesting option and is the driving force for the development of bio-refinery complexes. The overall goal of a bio-refinery is the integrated production of different classes of biofuels and biochemicals from various biomass feedstocks, through jointly applied conversion technologies [23,24]. Fast pyrolysis can indeed play an important role in bio-refineries; however, until now the role of pyrolysis in bio-refineries has remained limited. A new concept of the next generation bio-refinery should be developed by using the latest methods and engineering skills regarding process modelling, reaction planning, biomass chemistry, catalysis, and finally through a proper process integration and intensification. A pyrolysis-based thermo-chemical bio-refinery, such as the one shown in Fig. 1.1, could gradually change the structure of supply chains in the chemical industry, creating a need for innovative, sustainable chemistry solutions.

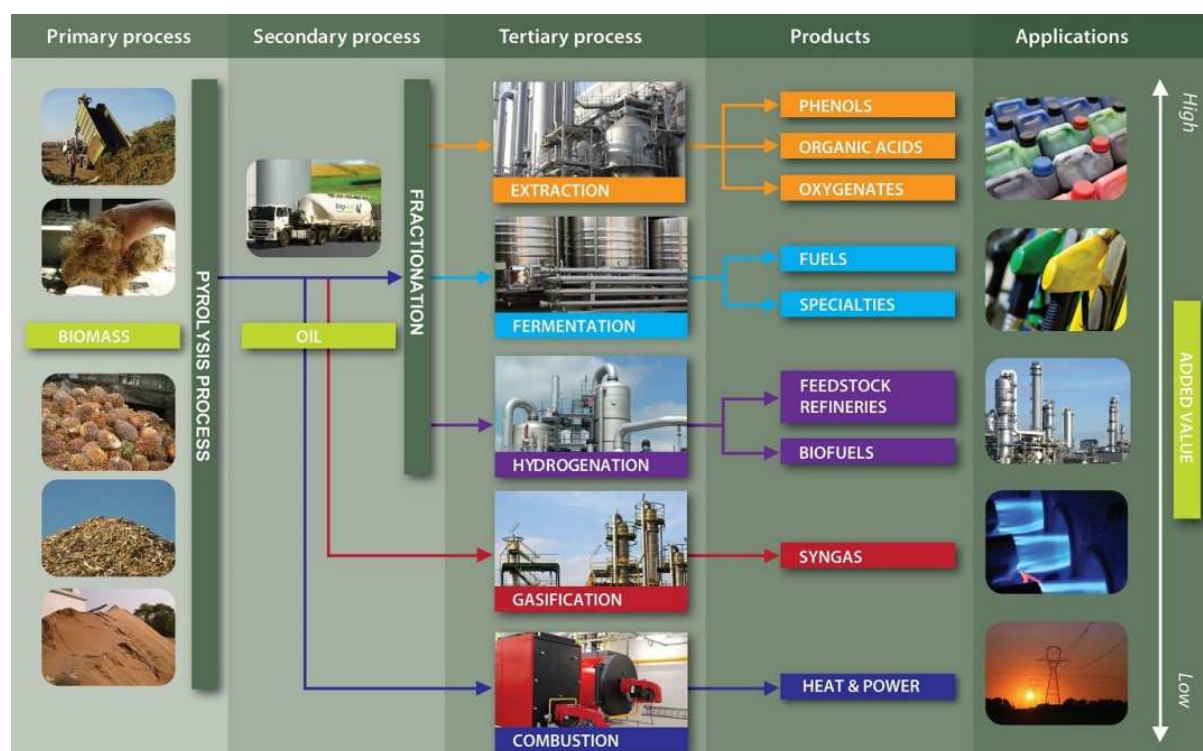


Fig. 1.1 Bioliquids refinery; BTG’s vision on a pyrolysis-based thermochemical bio-refinery, with permission from Robbie H. Venderbosch [25].

This thesis is focused on a further improvement of the process for biomass fast pyrolysis; viz. the catalytic fast pyrolysis of biomass. Both techniques will now be discussed briefly.

1.3.1 Fast pyrolysis of biomass

Fast pyrolysis is emerging as a cost effective thermo-chemical biomass conversion yielding a uniform, ash-free liquid product (*i.e.* crude bio-oil) that can be easily stored, transported and further processed. During fast pyrolysis of biomass, small biomass particles are rapidly heated up to moderate temperatures (400 – 550 °C [26]) in the absence of oxygen, and at atmospheric pressure. The exact yields and composition of the products depend on the biomass feedstock type, fast pyrolysis temperature, pressure, heating rate of the biomass particles, and the residence times of both the biomass particles and the released volatiles [27,28]. In the past, quite some attention was paid to optimize the process parameters of the fast pyrolysis process while aiming at high bio-oil yields. These are [29]:

- carefully controlled fast pyrolysis temperatures of *ca.* 500 °C,
- heating rates leading to a complete devolatilization of small biomass particles (*ca.* 3 mm [30]),
- short biomass residence times followed by rapid removal of produced char to minimize the cracking of volatiles,
- short volatile (*i.e.* vapours and aerosols) residence times of typically less than 2 s,
- rapid condensation of the released volatiles.

When these conditions are met, crude bio-oil is produced as the main product with yields of around 65 *wt.*% (dry-feed basis). The by-products of the process are a solid (char) fraction, and gaseous products (non-condensable gases). The yields of char and non-condensable gases are reported to be around 15-25 *wt.*% and 10-20 *wt.*%, respectively [12]. The bio-oil, char and non-condensable gases typically contain 70 %, 25 %, and 5 % of the energy in the biomass feedstock [29]. The fast pyrolysis process itself requires only about 15 % of the total energy contained in the feedstock, so the produced char and non-condensable gases can be used (by burning in combustors) to provide the energy for the process [29] (see also Chapter 7 in this thesis).

A careful selection and design of the fast pyrolysis reactor and the vapour condensation system (condenser) is crucial. A variety of reactor configurations have been developed and investigated; *viz.* circulating and bubbling fluidized beds, ablative, entrained flow, rotating cone, auger, and vacuum pyrolysis reactors [12,29,30]. For the details concerning the fast pyrolysis technology development, the reader is referred to the review of Venderbosch and Prins [30].

1.3.2 The need for bio-oil upgrading

The interest in the production of bio-oil has grown rapidly in recent years, due to the opportunities for:

- de-coupling of the fuel production (scale, time and location) from its utilization,
- easy handling of a liquid fuel in further processing (transportation, pressurization, atomization),
- the production of a renewable fuel for boilers, engines, turbines and gasifiers,
- upgrading of the pyrolysis liquids to a refinery feed or fuel blending components,

- integration in various biorefinery concepts, also for the conversion of lignin rich residues,
- separation of the minerals from the process to be returned to the soil as a biomass nutrient,
- the production of biochar (soil improver) as a by-product.

However, some adverse properties of crude bio-oil including its water content (15–30 %), the high oxygen content (35–40 wt.%), its corrosiveness (pH of 2–3), the low heating value if compared to fossil fuels (LHV of approximately 17 MJ/kg), poor volatility, and the presence of small particulates makes it unsuitable for the direct use as a transportation fuel or as a source for the production of fuels and chemicals [29,31]. Its immiscibility with hydrocarbon fuels and its chemical/thermal instability under storage and heating conditions further obstruct its direct use in almost any application [29,31,32]. Although the applications are still not all fully developed, bio-oil could in principle be used as a fuel for gasifiers, boilers, and turbines. For specific applications of bio-oil, like in diesel or gasoline engines, or as a bio-based feed material in the existing petroleum refineries, a certain degree of upgrading including the (partial) removal of oxygen and cracking of the oligomers present in bio-oil is required. However, the precise way of upgrading is not evident on beforehand, because it is closely related to the actual end-application. In case of engines, whether stationary (diesel generators) or mobile (car engines), upgrading has to be carried out with the primary objectives to:

- reduce the viscosity and instability,
- reduce the acidity, allowing the use of conventional injectors and pumps,
- prevent the formation of coke (avoiding plugging of injectors),
- increase the cetane number; this is an indicator for ignition behaviour in a diesel engine,
- improve the miscibility with conventional fossil fuels.

Although much effort has been put into for the development of fast pyrolysis with a maximum efficiency, throughput, and/or bio-oil yield, not much attention has been paid to the effect of the biomass composition and/or the fast pyrolysis conditions on the bio-oil composition [30,33]. Bio-oils contain a broad range of organic compounds and, hence, also offer the potential to be used as a renewable feedstock for the chemical industry for the production of high-value chemicals and liquid bio-fuels [12,30,33–35]. However, to realize these potential applications requires not only the maximization of bio-oil yield, but even more to control its chemical composition. Optimizing the yield of these specific component(s) or fraction(s) aimed at then becomes essential. This introduces severe constraints on both the biomass composition and the operating criteria. One of the few promising potential applications is the valorisation of the phenolics as building blocks of new synthetic bio-plastics, phenol-formaldehyde resins or epoxy- or polyurethane materials [35,36]. Bio-oils also have the potential to be used as a refinery feedstock for the production of bio-fuels [35,36] after being upgraded via hydrodeoxygenation (HDO) with pressurized hydrogen (mostly in the range of 30–140 bar [37]) over heterogeneous catalysts (*e.g.* CoMo- and NiMo-based catalysts). However, the economic viability of the HDO process strongly depends on

the amount of hydrogen consumed and requires control of the composition and the amount of the high molecular mass fraction (*e.g.* sugars) in the bio-oil. For the latter, catalytic fast pyrolysis seems to be an attractive alternative if a proper catalyst, the most suitable reactor technology, and the optimal process conditions can be identified; the clarification of this will be the main theme of this thesis.

1.3.2.1 Catalytic fast pyrolysis of biomass

(In this introduction, only a brief description on catalytic fast pyrolysis of biomass will be given. For in depth information, the reader is referred to the Chapters 2 and 7 in this thesis.)

It has been recognized already in the early days of fast pyrolysis R&D [38] that the application of catalysis could be of major importance in controlling the quality and the chemical composition of the bio-oil. As most of the bio-oil's adverse properties are caused by its highly oxygenated nature, bio-oil improvement basically refers to a reduction in the oxygen content (deoxygenation). For this purpose catalytic fast pyrolysis (CFP), which is a single step process that uses heterogeneous catalysts in the fast pyrolysis process, wherein the catalysts react with biomass derived pyrolysis vapours at atmospheric pressure [39], can be put in service.

In CFP, the heat transfer material, generally assumed inert in conventional fast pyrolysis, is (partially) replaced by a solid catalyst (*i.e.* in situ catalytic fast pyrolysis). The presence of the catalyst lowers the temperature of the pyrolysis process [40] and favours oxygen removal via decarbonylation (CO rejection), decarboxylation (CO₂ rejection), and dehydration (H₂O removal) reactions. Catalytic fast pyrolysis induces vapour phase reactions that cause a change in oxygen functionalities, alleviate the acidity, increase the calorific value, and improve the stability of the produced liquid product (predominantly organic phase, *i.e.* CFP-oil). Hence, the CFP-oil becomes more similar in chemical composition to current gasoline and diesel fuels than the conventional bio-oil [41,42].

The product distribution in CFP and the ultimate composition of the CFP-oil is influenced by the operating temperature of the catalyst, the type of the biomass feedstock, residence time and the heating rate of the biomass, the catalyst-to-biomass ratio (or weight hourly space velocity, WHSV), vapour residence time, and the type of the catalyst (including pore size, acidity, nature of active sites, and the presence of metals). The success of the operation depends on the precise optimization of these parameters.

In CFP of biomass, the selection of an appropriate catalyst is crucial for the formation of higher value compounds (phenolics, alkanes, monoaromatic hydrocarbons, *etc.*) and for the elimination of undesirable compounds (acids, ketones, poly-aromatic hydrocarbons, *etc.*) [43,44]. Lifetime, activity at various temperatures and other process conditions, deoxygenation performance, and the capability to suppress the formation of coke are important issues in the catalyst selection process. Zeolites, and particularly ZSM-5, were shown to be effective in the conversion of biomass to reasonable yield of aromatics [45] and in the selective deoxygenation of pyrolytic vapours thereby increasing the C/O ratio [46,47]. The use of zeolite cracking catalysts also leads to smaller molecules being formed, due to

cracking of the high molecular weight molecules present in the primary pyrolysis vapours [48,49].

1.4 Outline of the thesis

While the literature on the catalytic fast pyrolysis of biomass is rapidly expanding, the translation of laboratory results to viable process concepts and pilot plant trials remains scarce. The present thesis discusses the catalytic fast pyrolysis of lignocellulosic biomass in a process oriented way that may initiate a useful process technology development in the near future. The final goal is to come up with some recommendations and suggestions on how to realize this technique at a commercial/industrial scale. That requires a better understanding of the precise effects of the essential process parameters (*e.g.* catalyst-to-biomass ratio) and design elements (*e.g.* reactor type, catalyst type) on the one hand, and definitions and outcomes of possible obstacles (*e.g.* successive regeneration of the catalyst, effect of biomass ash) on the other.

Chapter 2 provides a review of catalytic fast pyrolysis summarising the achievements and the potentials of the methodology. It covers the existing literature dealing with laboratory research mainly but also reporting some commercial/industrial developments. The current status of research is provided, while focusing on the detailed overview of the suitable process parameters and reactor technologies, specific catalyst types employed, as well as on the reaction mechanisms. It further includes an outlook for the commercialisation of the technology.

The first part of the experimental work (Chapter 3 and Chapter 4) is concerned with the operation of a fully controlled, continuously operated fast pyrolysis mini-plant (0.5 kg/h intake) based on auger reactor technology. In all experiments, pine wood was used as the biomass feedstock. This mini-plant was designed to allow three types of biomass fast pyrolysis experiments, *viz.* non-catalytic, in situ catalytic fast pyrolysis and ex situ upgrading of non-catalytic fast pyrolysis vapours by means of a downstream, moving-bed catalytic reactor. The mini-plant allows a stable operation under a wide range of process conditions to maintain high mass balance closures and good reproducibility of the experiments.

In **Chapter 3**, the validation of the abovementioned set-up was studied. The performance of the system was verified by in- and ex situ applications of a single type of heterogeneous ZSM-5 based acidic catalyst while the non-catalytic results were taken as reference.

For the first time in the catalytic fast pyrolysis literature up to date, the screening of metal doped (and their parent counterparts) heterogeneous catalysts in in situ *continuous* catalytic fast pyrolysis of pine wood was studied in **Chapter 4**. In total, eight proprietary catalysts were tested. They were divided into three groups based on their acidity, type of carrier, the active metal contents, and according to being aged or fresh. The main objective of this study was to find the best performing catalysts capable of retaining the amount of the organic liquid products as much as possible with a minimum water production, and also

achieving an effective reduction of the acidity during in situ catalytic fast pyrolysis of pine wood. The catalysts were also tested on a micro-scale using a py-GC/MS system.

The second part of this thesis was concerned with the design, construction, and operation of a fully controlled, continuously operating lab-scale pyrolysis set-up (0.2 kg/h intake). This set-up was designed based on the bubbling fluidized bed technology and allows non-catalytic and in situ catalytic pyrolysis experiments. The unique feature of this reactor is that it contains a specially designed mixer (agitated bed) that ensures a uniform mixing of the bed contents (catalyst and sand) without any segregation. The research discussed in **Chapter 5** was meant (1) to validate the reliability of this set-up by multiple repetitions of non-catalytic and catalytic (in situ) pyrolysis experiments for pine wood at 500 °C under identical conditions, and (2) to investigate the effect of a repeatedly regenerated ZSM-5-based catalyst (eight reaction/regeneration cycles in total) on the yields and compositions of the pyrolysis products in relation to the applied process conditions and on the catalyst itself.

Most of the studies in CFP literature are dealing with fresh catalyst whereas in large-scale practical applications, the spent (and coked) catalyst is regenerated (subjected to combustion) and then returned to the pyrolysis process [50]. Although this is pretty much similar to the FCC process in an oil refinery, one aspect that is different – and thus far not properly understood – is that biomass also adds mineral matter (or ash) to the process. Through successive cycles of pyrolysis and catalyst regeneration, a considerable amount of this ash accumulates and could potentially affect the chemistry of pyrolysis as well as the stability and/or the activity of the catalyst. Hence, in order to understand the role of indigenous and added inorganic compounds in CFP of biomass, and the potential ash/catalyst interactions that may take place in CFP, the influence of them on the distribution and composition of products resulting from the primary and secondary fast pyrolysis reactions has been examined in **Chapter 6**. The effects of biomass ash and its major constituents on the pyrolysis product yields and composition as observed in the non-catalytic and catalytic fast pyrolysis of pine wood are reported in this chapter. A discussion is provided on whether catalyst deactivation is merely caused by coke deposition and thermo-mechanical, chemical and structural changes of the catalyst, or by the presence of the biomass ash as well.

In **Chapter 7**, an extensive discussion regarding the efficient and the economical use of primary and secondary products of catalytic fast pyrolysis process is given and operational barriers for the implementation of catalytic fast pyrolysis technology is provided. Moreover, the state-of-art of the CFP technology, the best suited process modes/parameters, and proper heat integration was reviewed. Some process alternatives for efficient CFP operation are suggested as well.

Finally, the summary, main conclusions, and remarks are presented.

Chapter 2

Achievements and potentials in catalytic fast pyrolysis of biomass

This chapter provides a review of catalytic fast pyrolysis of lignocellulosic biomass and summarises the current status and the achievements in the research and development of the technology based on the existing literature and the commercial/industrial attempts. It addresses the types of biomass used, overview of the applied process parameters and reactor technologies, and the specific catalysts employed. The current understanding of the chemistry and the reaction mechanisms in catalytic fast pyrolysis of biomass is provided as well.

2.1 Introduction

Large-scale industries based on crude oil processing that supply transportation fuels, fine chemicals, polymers, *etc.* are spread all over the world. However, the finite nature of crude oil, the deterioration of the environment caused by its use, technical (*e.g.* BP Deepwater Horizon disaster in 2010) and security related risks [4] of its supply are the main problems linked with the continued use of crude oil. Such problems demand a transition from today's fossil based economy to a more sustainable one based on renewable resources for energy and chemicals. Renewable energy sources by which mostly heat and power is produced (*i.e.* solar, wind, hydropower, *etc.*), are not suitable for the production of conventional transportation fuels and raw materials (*e.g.* petroleum based chemicals) used in the current industries [40]. Thus, to contribute to the sustainability of the current petro-chemical economy and to continue the production of petroleum-like products, chemicals and (transportation) fuels, biomass may be put in service. Due to its abundance and fast turnover in organic carbon and hydrogen, there is recently a growing interest in biomass as an alternative for the currently used non-renewable fossil resources. Biomass can be converted via thermo-chemical processes (*i.e.* pyrolysis, gasification) to fuel intermediates and chemicals in liquid, solid, and/or gaseous forms and potentially replace fossil fuels, either fully or in blends of various fractions. This makes biomass the most promising source for renewable energy and chemicals with an increasing potential for the worldwide biofuels and biochemicals market [47,51].

Ideally, the production of fuels and/or chemicals from solid biomass materials would include a single process step with a high degree of conversion. The flexibility in using various types of biomass feedstock and short feedstock conversion times could be the assets of the process. Pyrolysis has been considered as a viable biomass conversion technology for the production of fuel intermediates, chemicals, and heat sources in the form of liquid, solid, and gaseous product fractions in various proportions. It is defined as the direct thermal decomposition of an organic substance (*e.g.* woody or residual biomass, waste plastic, *etc.*) at elevated temperatures (between 250 and 650 °C) and atmospheric pressure in the complete absence of an oxidizing agent (air or oxygen); so that oxidation, combustion, or gasification do not occur to any appreciable extent. Compared to some other biomass-to-biofuel conversion processes, a major advantage of pyrolysis is that any type of biomass feedstock can be processed [52].

The outcome of a pyrolysis process depends on several factors related to the type and the properties of the biomass feedstock and the reactor, process conditions, and intended application of the final products [28] (Table 2.1). When large (*ca.* 100 mm) solid wood pieces are heated slowly (*ca.* 0.1–1 °C·s⁻¹ [53]) to temperatures between 200–300 °C with residence times of few minutes to hours, solid yields as high as *ca.* 70–90 wt.% on feed basis are obtained. This process is known as torrefaction and the solid product is called torrefied biomass. On the other hand, in slow pyrolysis or carbonization, the application of higher temperatures (400–500 °C) with similar heating rates to that of torrefaction results in 30–33 wt.% of solid product (*i.e.* char) [54]. In order to maximize the yield of liquid product, pyrolysis has to be conducted at temperatures of *ca.* 500 °C, and at higher biomass heating rates. Residence times of 2 to 20 seconds are needed for the complete devolatilization of small

biomass particles (of a few millimetres in diameter) followed by rapid quenching of released vapours (short vapour residence times of *ca.* 1 s). This type of pyrolysis process is called fast pyrolysis. The main product, bio-oil (referring to crude, non-catalytically produced single-phase pyrolysis liquid), can be obtained in yields of 60 to 70 wt.% (on a dry-feed basis) in continuously operated pilot plants and in laboratory reactors. In the literature, bio-oil yields over 70 wt.% obtained in laboratory-scale reactors are reported. However, these are exceptional and only possible for well-defined feedstock (*e.g.* cellulose, glucose, xylan, furan, *etc.*) under precisely controlled process conditions [30]. On the other hand, when the vapour residence times are kept longer (*ca.* 10–30 s), this process is called as the intermediate pyrolysis. The outcome of this process is a two-phase liquid product with a yield of *ca.* 50 wt.%, together with 25 wt.% for both char and the non-condensable gases [29].

Table 2.1. Typical product weight yields (dry wood basis) obtained by different modes of pyrolysis of wood (Adopted from Bridgwater [29]).

Mode	Conditions	Liquid	Solid	Gas
Fast	~500 °C, short vapour residence time ~1 s	75%	12% char	13%
Intermediate	~500 °C, vapour residence time ~10–30 s	50% in 2 phases	25% char	25%
Carbonisation (slow)	~400 °C, long vapour residence time of hours to days	30%	35% char	35%
Torrefaction (slow)	~290 °C, solids residence time ~10–60 min	0% unless condensed, then up to 5%	80% solid	20%
Gasification	~750–900 °C	5%	10% char	85%

Fast pyrolysis has the advantage over other thermo-chemical conversion options (*e.g.* gasification, and direct liquefaction [55]); it produces comparatively high yields of liquid for direct combustion (for heat and power generation). Besides, it can be applied as an intermediate pre-treatment step, where solid biomass is transformed into a liquid with higher energy density compared to the original feedstock. Eventually, the resulting pyrolysis liquid can be easily transported and/or stored. The by-products of the process are char and non-condensable gases (NGC's) which contain typically 25 % and 5 % of the energy in the feed material, respectively [28]. In order to provide the endothermic reaction heat necessary for pyrolysis reactions (*ca.* 1.5 MJ/kg dry wood [21]), these by-products can be burnt externally (for biomass drying, co-combustion, *etc.*) or in the process (see Chapter 7 in this thesis). For a detailed description of fast pyrolysis technology and recent advances in related research, the reader is referred to some previously published reviews [27,29,30,56].

Crude bio-oil is a complex and homogeneous mixture of water and a large number of mainly oxygenated chemicals (30–40 wt.% [57]). The molecular weights of the organic macromolecular lignocellulosic degradation products range from that of light hydrocarbons up to 5000 g/mol or more (pyrolytic lignins, sugar oligomers) [12,58,59]. The organic chemicals in crude bio-oil can be classified into four main categories: 1) anhydrosugars, 2)

furan derivatives, 3) low molecular weight oxygenates (*e.g.* carboxylic acids, ketones, aldehydes), and 4) phenols and aromatics [60]. Without any modification, this mixture of chemicals could be used as feed for boilers, turbines, engines, and gasifiers. However, its water (15–30%) and oxygen content [61], strong corrosiveness (pH of 2–3), high viscosity (35–1000 cP at 40 °C), low heating value (16–19 MJ·Kg⁻¹, around half of that of petroleum fuels), poor stability (viscosity and phase change in time), poor volatility, limited miscibility with hydrocarbon fuels, *etc.* makes crude bio-oil unsuitable to be served as feed into existing petroleum-based refinery units for the production of liquid (transportation) fuels and chemicals [29,31]. In order to overcome the aforementioned drawbacks of crude bio-oil, improvements in its quality can be achieved through actions (individual or in combination) before, during or after the pyrolysis step. These can be the demineralization of the feed by an acid wash (leaching), staged condensation to lower the acid and water content of crude bio-oil, catalytic upgrading of the produced bio-oil (*e.g.* hydrodeoxygenation), or the application of heterogeneous catalysis within the pyrolysis process (*i.e.* catalytic pyrolysis) [26]. The common target of all possible bio-oil upgrading techniques must be to favour the pathways towards reducing the oxygen content (*i.e.* deoxygenation) while cracking the large aromatic structures to smaller ones [31,62]. This results in an upgraded bio-oil with increased stability, higher heating value, and miscibility with petroleum refinery feedstock and/or petroleum-based fuels.

In the last decade, many pyrolysis researchers have focused their attention to two main technologies for improving crude bio-oil [63] to enable the production of certain chemicals (*i.e.* hydrocarbons, phenols, aromatics) and/or liquid fuels or fuel intermediates similar in physical and chemical properties to current gasoline and diesel fuels. Hydrodeoxygenation (HDO) is a downstream upgrading process for pyrolysis liquids which is based on the hydrotreatment of bio-oil over heterogeneous catalysts (*e.g.* CoMo- and NiMo- based catalysts) under high hydrogen pressure (mostly in the range of 30–140 bar [37]) and at elevated temperatures (330–450 °C) [64–66]. Alternatively, heterogeneous catalysis (*i.e.* zeolites) can be used directly inside the fast pyrolysis reactor (catalytic fast pyrolysis, CFP). The target of CFP is to enhance the cracking reactions of the heavy molecules in the primary pyrolysis vapours as well as to induce deoxygenation reactions to eliminate oxygen from the resulting bio-oil [42]. In terms of capital and operational costs, CFP seems more economical since it is a single step ‘biomass-to-liquids’ process and does not require the supply of expensive high pressure hydrogen gas [67,68]. Although both techniques exhibit major operating problems (*e.g.* reactor plugging, rapid catalyst deactivation) and low yields of liquid fuels [69], it was stated that catalytic fast pyrolysis has several advantages over other techniques [70]. These advantages are; to achieve all of the targeted chemistry in a single reactor with the use of inexpensive aluminosilicate catalysts, the possibility to process a range of different lignocellulosic feedstock with only simple pre-treatment (*e.g.* grinding, drying), and the possibility to blend the liquid product as a feedstock (or co-feedstock) into the existing gasoline infrastructure. Hence, the main target of catalytic fast pyrolysis process should be to retain as much carbon and hydrogen in the liquid product as possible while removing the highly reactive oxygenated species (*e.g.* organic acids, carbonyls) [71]. In order to produce a high-quality liquid product in sufficient quantities (CFP-oil), various aspects of

the CFP process, ranging from biomass feedstock selection (woody biomass, forestry or agricultural residues, *etc.*), reactor types (bubbling/circulating fluidized beds, auger reactors, *etc.*), catalyst types (microporous or mesoporous zeolites, metal oxides, *etc.*) and the process conditions (temperature, vapour residence time, catalyst-to-biomass ratio, *etc.*) [46] must be well-optimized.

In recent years, catalytic fast pyrolysis of biomass has been extensively studied and various literature reviews have been published [40,47,60,63,72–75]. The objective of this comprehensive review is to focus on the R&D advances and trends in the field of catalytic fast pyrolysis of woody biomass over micro- and meso-porous acidic zeolites, basic and metal catalysts based on the large number of literature reports published since 1995 up to date. Prominent research in this area will be summarized with their key features highlighted. The main spotlight will be on the research aimed to achieve the optimal biomass feedstock and catalysts, reactor technologies, and process conditions. The current understanding of the chemistry and the reaction mechanisms in catalytic fast pyrolysis of biomass is provided as well.

2.2 Process optimization for catalytic fast pyrolysis of biomass

In general, five major factors influence the CFP process:

- the type and the properties of the biomass feedstock,
- the process parameters (*i.e.* temperature, heating rate, catalyst-to-feed ratio, vapour residence time, *etc.*),
- the choice of the reactor technology,
- the operation mode (*i.e.* in- or ex situ),
- and the type of the catalyst used.

The success of the process is closely related to the precise optimization of these factors which would yield a maximum quantity of catalytic fast pyrolysis oil (CFP-oil) with the desired quality, while the amounts of by-products (*i.e.* char, coke on catalyst, and non-condensable gases) are minimized. To achieve this target, a remarkable research effort has been shown in the last two decades by researchers all over the world. In attempt to provide an overview and summarize the trends in CFP research, the distribution of the literature publications regarding catalytic fast pyrolysis of lignocellulosic biomass (published between 1988 and 2014) is given in Tables A.2.1 and A.2.2 in the Supporting Information. These tables are organised based on the operation mode, the reactor type and the biomass feedstock type.

2.2.1 Types and properties of biomass feedstock

Lignocellulosic biomass, referring most of the plants or plant-based materials, is composed of three main structural constituents (*i.e.* cellulose, hemicellulose and lignin), and some non-structural components (minerals, extractives, moisture), *viz.* in varying weight percentages depending on the type of biomass [74,76]. The relative proportions of cellulose, hemicellulose, and lignin in the biomass feedstock have a distinct effect on the quality and the quantity of the produced bio-oil [77]. Especially during the screening of potential catalysts for CFP, it is essential to relate the thermal degradation mechanisms associated with the conversion of these constituents individually [75]. This would help to understand the complex nature of the bio-oils. When the target of CFP is the production of certain chemicals (*i.e.* aromatics, phenols, olefins) in high yields, model compounds can be studied to reveal the reaction mechanisms and develop an understanding of any catalytic factors which may influence the overall reactions [70]. This may help in designing CFP catalysts.

According to the U.S. Department of Energy [78], biomass feedstock can be classified into three families: forestry, agriculture and municipal. At the research level, hundreds of biomass materials have been screened [12,79] and they can be classified as: woody (soft and hard woods, forest residues, sawdust), agricultural residues (husks, stalks, stovers, straws), industrial by-products (fruit skins and seeds, lignin), non-woody (grass), waste products (sewage sludge, animal litter) and marine (seaweeds) [77]. In case of conventional pyrolysis, different types of biomass feedstock result in varying bio-oil yields [67,75] depending on their biomass constituents (*i.e.* cellulose, hemicellulose, and lignin) and ash contents. In case of CFP however, high lignin (because of its lower oxygen content and the presence of aromatic moieties in it) and low ash containing biomass feedstock are preferred. Compared to other types of biomass feedstock, woody biomasses contain a higher amount of lignin [80] and thus yield a bio-oil with higher heating value. On the other hand, agricultural residues and non-woody biomass have higher ash contents. These high ash containing biomass feedstock are less desirable for CFP because of the catalytic effect of ash under pyrolysis conditions [29,81] (see Chapter 6 in this thesis). Ash may favour the formation of water and gas at the expense of liquid organics and inhibit the activity of the catalyst by poisoning it. Moreover, due to their higher hemicellulose content compared to that of woody biomass feedstocks, agricultural and non-woody biomass feedstock produce more char and gas in pyrolysis. Generally, woody biomass feedstock was seen to produce the best quality bio-oil in terms of C, H and water content [77]. Until now, low-ash containing woody biomass seems to be the most ideal biomass feedstock for industrial scale production of higher quality bio-oil via CFP. Tables A.2.1 and A.2.2 in the Supporting Information also show that woody biomass has been used in most of the studies due to the fact it is easy to process (*e.g.* handling and feeding), and well characterized (especially for some specific wood types, such as pine and beech).

2.2.2 Process parameters

2.2.2.1 Temperature

In pyrolysis, the *temperature* strongly influences the yield distribution and the physical/chemical properties of the products (*e.g.* carbon content, oxygen content, pH, and viscosity of bio-oils) [82]. Since the thermal degradation reactions of biomass occurring during pyrolysis are endothermic, the decrease in pyrolysis temperature implies a decrease of the input energy for the system, which is beneficial from an energetic and economical point of view. In CFP, the reaction temperature is the most critical process parameter that affects the relative rate of the catalysed vapour phase reactions [40]. Catalysis in CFP is known to have a lowering effect on the reaction temperature; however, the precise mechanism is still unclear at present [60].

2.2.2.2 Residence time and heating rate of biomass

Catalytic fast pyrolysis of biomass involves various chemical reactions in the vapour phase. In order to design a cost-effective commercial CFP technology, modelling of these complex kinetic processes is necessary [40]. However, heat and mass transfer limitations prevent an accurate representation of these reactions by chemical equilibria [83]. In that respect, Pyrolysis number (Py), which compares internal heat conduction transfer and chemical kinetics [84] and/or Damköhler numbers (Da), which relate the chemical reaction timescale (reaction rate) to the transport phenomena rate occurring in a system could be taken into account. In the presence of a catalyst, high biomass heating rates ($>500\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$) are needed to avoid coke formation (see Fig. 2.5) by homogeneous thermal decomposition reactions, and to produce high grade bio-oil and gasoline range compounds. On the other hand, for heating rates above $50\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$ in the presence of a zeolite catalyst, the aromatic selectivity was shown not to be a function of the heating rate but for the lower values it was [85].

In CFP of biomass, biomass residence time simply refers to the run time (t_{run}) for batch reactors. However, in flow-through or continuous reactors, biomass residence time refers to the time that the biomass particles spend in the hot reactor zone. Being closely related with the biomass particle size, the residence time and heating rate of biomass together affect the degree of devolatilization and play a major role in defining the reaction products and the product distribution (see Section 7.3.1.3 of Chapter 7 in this thesis).

2.2.2.3 Catalyst-to-biomass ratio

If the catalyst in the reaction zone is deactivated (*e.g.* coking, fouling, attrition, *etc.*) before all the released primary pyrolysis vapours are being reformed by the catalysis, the produced bio-oil will be a mixture of non-catalytic bio-oil and CFP-oil. This is also valid for very short vapour residence times that prevent the sufficient contact necessary for the reactions on the catalyst surface. Hence, high *catalyst-to-biomass ratios* are necessary to ensure the adsorption of the primary pyrolysis vapours on the catalyst surface with a broader distribution. In this way, these vapours can interact with the catalyst before they thermally decompose to coke via the secondary reactions or before being quenched in the condenser

system. When the catalyst has a high acidity, high catalyst-to-biomass ratios have been reported to suppress coke and PAH forming polymerization reactions to a higher degree [86,87]. Another term frequently used in the case of CFP is the weight hourly space velocity (WHSV, h^{-1}). WHSV, defined as the ratio of the mass flow rate of feed (in g/h) to the mass of catalyst (in g), is one of the most important variables in CFP. The variations in WHSV may affect the yield of CFP-oil and the formation of water [82].

2.2.2.4 Vapour residence time

Another important parameter in fast pyrolysis (either catalytic or non-catalytic) is the *vapour residence time*. In CFP, the vapour residence time needs to be carefully controlled since the catalysed reactions resulting in the volatile chemical species and the liquid intermediates are not kinetically equilibrium controlled. If not carefully controlled, these intermediates may undergo secondary reactions that may be catalysed by the biomass originated alkali and alkaline earth metals (AAEMs), with the catalyst to form heterogeneous coke, or take place as homogeneous reactions in vapour phase [40,26]. Hence, short vapour residence times (< 2 s [88]) in the heated zone (including the reactor zone) followed by rapid quenching of these vapours is crucial. Careful optimization of the carrier gas flow rate is also necessary to achieve the balance between the time necessary for the completion of catalytic reactions and the suppression of unwanted secondary vapour phase reactions.

Overall, for an optimal CFP process resulting in sufficient yields of an organic fraction (CFP-oil) with improved quality, carefully optimised reaction temperatures, high heating rates, a biomass residence time sufficient for a complete devolatilization, optimal catalyst-to-feed ratios, high levels of WHSV (>1 h^{-1}), fast separation of the solids (*i.e.* char), short vapour residence times (<2 s), and fast quenching of the produced vapours are all necessary [46,82,89,90].

2.2.3 Reactors used in CFP of biomass

In pyrolysis processes, the reactor is the core and generally the most researched part of the fast pyrolysis technology in terms of an engineering point of view. As summarized in Tables A.2.1 and A.2.2 in the Supporting Information, a large body of literature is available for CFP of biomass carried out at both bench/lab scale (*i.e.* bubbling and circulating fluidized beds, conical spouted bed, auger reactor) and analytical scale reactors (*e.g.* analytical pyrolysis setups or py-GC/MS, packed (fixed) bed, tubular quartz micro reactor). In these studies, the performance of various catalysts on product yields and characteristics have been investigated. Nevertheless, it is crucial to note here that the results obtained are difficult to compare because of the variety in the reactor types, the scales of the reactors, and the process parameters used.

2.2.3.1 In situ and ex situ processing in CFP of biomass

Based on the location of the catalyst in the process, catalytic pyrolysis can be divided into two different operation modes: in situ and ex situ [75] (Fig. 2.1). In the in situ process mode, a pure catalyst or a catalyst-sand mixture replaces the heat carrier which is typically pure sand in a traditional, non-catalytic fast pyrolysis. The catalytic fast pyrolysis then occurs in a single reactor where biomass feedstock and the catalysts are mixed intensively to enable a good contact between the two. Generated primary pyrolysis vapours instantly diffuse into the catalyst pores where the catalytic cracking/reforming reactions occur. In small scale laboratory reactors, such as analytical pyrolysis and packed (fixed) beds, catalyst and powdered biomass are mixed and the mixture is placed in a tube with the aid of a ceramic (or quartz) wool, or a sintered disc support [40,64]. When in situ processing is applied in continuously operated larger scale units (*i.e.* circulating fluidized bed, auger reactor) the char should always be separated before the catalyst regeneration step (see Chapter 7 in this thesis). Although practically hard to implement, the reason for this crucial separation is to prevent the accumulation of char-bound ash (minerals) on the active surface of the catalyst material; because in the case of CFP of biomass, negative effects of biomass ash on the bio-oil yield and quality have been observed [29,81] (see Chapter 6 in this thesis).

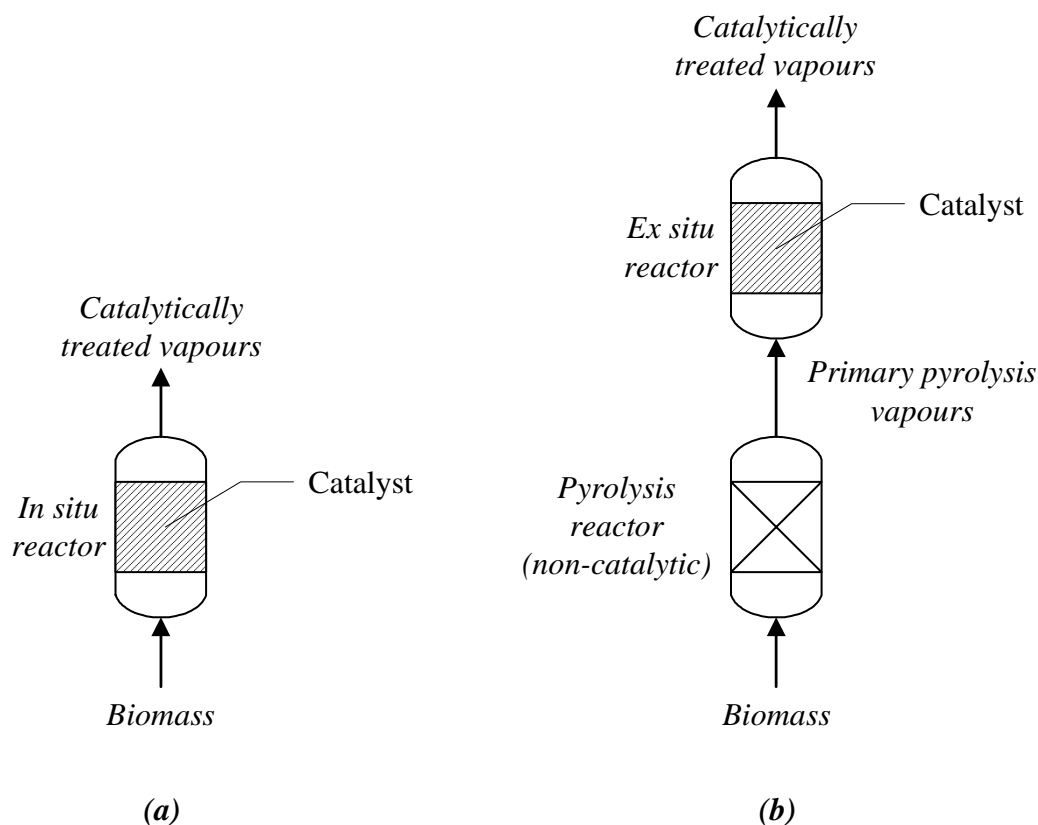


Fig. 2.1. Sketch showing the difference between two operation modes in CFP: (a) in situ, and (b) ex situ.

In the *ex situ* mode, the non-catalytic pyrolysis vapours produced in the primary (pyrolysis) reactor are carried through a secondary (moving bed, or circulated transported bed) reactor where they are contacted with the catalyst. One of the biggest advantages of the *ex situ* processing is that the temperatures of both reactors are independently adjustable, which assists in controlling the product distribution and selectivity [75]. Moreover, *ex situ* processing allows the possible secondary input of gas (*e.g.* steam, hydrogen) to the *ex situ* reactor; this might improve the catalytic processing [40]. The contact time between the primary pyrolysis vapours and the catalyst should be carefully controlled for a complete reforming. *Ex situ* catalysis can be applied in a separate fixed/packed bed in the form of pellets or monoliths. This avoids the damage due to catalyst particle attrition that may readily occur in a circulating transported bed; it can severely limit the catalyst lifetime [40]. The char formed inside the pyrolysis reactor can be further combusted in order to provide the heat needed for the pyrolysis process [91]. Hence, unlike in the *in situ* operation mode, the periodic regeneration of the spent catalysts (refers to the removal of the coke on catalyst by oxidative treatment) can be conducted in the absence of char, and thus the accumulation of biomass ash (mainly within the char structure) in the catalytic reactor can be prevented. Adversely, the need for an additional catalytic reactor (or two additional reactors operating sequentially in operation and regeneration modes) increases the capital and operating costs to a great extent which can be considered as the main drawback of the *ex situ* processing. Moreover, the additional vapour residence time in such a system may cause further secondary reactions and promote the undesired water and coke production. This could decrease the quality and the quantity of the liquid product. For more detailed information regarding the process modes the reader is referred to Chapter 7 in this thesis.

2.2.3.2 Laboratory and pilot scale reactors for CFP of biomass

Fluidized bed reactors are widely used for biomass fast pyrolysis. They are applied also in a vast number of industrial processes due to their excellent mass and heat transfer characteristics, scalability and simplicity of operation [72,92]. In laboratories, they have been frequently used for non-catalytic and catalytic biomass fast pyrolysis due to their ability to provide high biomass heating rates, high catalyst-to-feed ratios [85], and high bio-oil yields. In case of CFP, biomass is fed into a hot fluidized bed reactor, where it thermally decomposes to form primary pyrolysis vapours. These vapours are then contacted with the catalysts, either *in-* or *ex situ*, and soon condensed to form an upgraded liquid product (CFP-oil).

In CFP literature, two types of fluidized bed technologies have been used in laboratories, namely bubbling and circulating fluidized beds. Bubbling fluidized beds (BFBs) can be considered as ‘semi-batch’ reactors in which all the solid bed material (*i.e.* catalyst, sand) stays together during the operational run time without being transported outside the reactor bed. While being quite suitable in the lab for conventional non-catalytic biomass pyrolysis, BFBs are less ideal for CFP because the bed material needs to contain a certain amount of catalyst. With the start of continuous feeding of the biomass feedstock, the deactivation of the catalyst takes place within a very short time. Consequently, the catalyst behaves as an inert material for the rest of the operation. A BFB reactor could also be used for the *ex situ* upgrading of non-catalytic pyrolysis vapours when being placed after the primary

pyrolysis reactor. However, catalyst deactivation would again be a serious issue requiring the catalyst to be refreshed continuously, either by feeding fresh catalyst or by recycling a regenerated catalyst [69]. This can be solved by the application of two parallel ex situ reactors operating sequentially in an active and in a regeneration mode.

Another drawback of bubbling fluidized beds in case of CFP is the change in the fluidization behaviour when a catalyst is added to the bed material (*e.g.* sand-catalyst mixture). Typical inert solid materials such as Al_2O_3 , SiO_2 , and sand used in BFB reactors have higher densities and bigger particles than zeolite catalysts (*e.g.* FCC, ZSM-5). A bed material mixture composed of Geldart's class B and C particles [93] cannot be fluidized together. It would quickly result in segregation and excessive entrainment of the fine catalyst particles. Because relatively high fluidization velocities are required to limit the vapour residence times, the BFB is unsuitable for CFP. Commercially available catalysts have high porosities and small particle diameters; they are designed particularly for the applications in circulating fluidized beds. To overcome this problem in our laboratory, we developed a reactor (similar in design to the conventional BFB reactors) in which a mechanical mixer continuously agitates the bed contents (details can be found in Chapters 5 and 6 of this thesis). This way, the bed contents remain well mixed without any risk of particle segregation. However, since the bed material is not continuously replaced, catalyst deactivation, as previously explained, still occurs in our laboratory setup, which is the subject of investigation.

Circulating fluidized bed (CFB) including a regeneration step for the continuous catalyst regeneration seems the most appropriate technology for CFP of biomass. In CFB reactors, char and the bed material (*i.e.* catalyst) coming from reactor bed are separated from the pyrolysis vapours and gases by cyclones, and transferred over the top to a combustion reactor (*e.g.* regenerator) [94]. In contrast to lab-scale bubbling fluidized bed reactors where the catalyst stays in contact with the biomass originated char (containing most of the biomass ash) during the operational run time without being regenerated, circulating fluidized bed technology offers a few seconds of contact (retention) time (<1 s [32]) between the catalyst and the biomass. By the frequent regeneration, the catalyst should in theory retain most of its original activity and contact the freshly-fed biomass always in an active state [72,86]. Unlike in BFB reactors, high fluidization velocities in CFB's are not a problem for the small catalyst particles, as both the char and the catalyst are meant to be passed through the cyclones.

Currently, a considerable interest exists in using auger reactors both for research and industrial use [95]. Auger reactors offer some distinct advantages such as high heating rates when heated by an externally supplied heat carrier, being compact and robust, less consumption of carrier gas, feedstock flexibility and anticipated processing capacities from 50 to 100 tons/day [95–97]. Practically, the biomass feedstock and the heat carrier stay in contact on the auger screw for a time necessary to complete the biomass devolatilization. Solids (heat carrier and char) and pyrolysis vapours are then physically separated at the end of the screw. Continuously fed biomass feedstock is always brought into contact with fresh (or regenerated) catalyst, which makes the auger reactor technology quite suitable for CFP.

Several researchers have performed catalytic pyrolysis in laboratory and small scale reactors. Table 2.2 shows the product yields obtained from laboratory and pilot scale reactors

for catalytic fast pyrolysis of woody biomass feedstock using microporous zeolites (*i.e.* ZSM-5) (the process conditions of these studies can be found in Tables A.2.3 and A.2.4 in the Supporting Information). Zeolites are known to be effective in cracking, deoxygenation, and synthesis of aromatic hydrocarbons [44]. The reason this catalyst has been selected was that the majority of the previous studies concerning the upgrading of biomass pyrolysis vapours were performed with this type of catalyst. Most of these studies were carried out in semi-continuous mode by using bubbling fluidized bed reactor technology. Here, semi-continuous operation refers to the continuous biomass feeding into a stagnant bed of catalyst (or catalyst-sand mixture). Besides, the circulating fluidized bed, auger and conical spouted bed have been applied, particularly for continuous CFP. Recently, Jae *et al.* developed a unit with continual catalyst addition and removal based on bubbling fluidized bed technology (entry no.9 in Table 2.2, entry no.15 in Table A.2.3) [98]. Olazar and co-workers reported the catalytic pyrolysis of sawdust in a conical spouted-bed reactor by using a HZSM-5 catalyst [99] (entry no.12 in Table 2.2, entry no.34 in Table A.2.3); for details see Section 2.3.2.1.2. In this reactor setup, the bottom section of the reactor is conical in shape and a high velocity stream of gas (the spout) induces circulation within the catalyst bed. Circulating fluid beds with continuous catalyst regeneration system have been used for CFP by Lappas and co-workers at CPERI (entry no.10 in Table 2.2, entry no.9 in Table A.2.3) [64,32]. For this thesis, we conducted continuous in- and ex situ catalytic fast pyrolysis of woody biomass (pine wood) based on auger reactor technology by using a ZSM-5 based FCC catalyst (entries no.11 and no.15 in Table 2.2, entry no.33 in Table A.2.3, entry no.20 in Table A.2.4) [100] (see Chapter 3 in this thesis).

Table 2.2. Product yields obtained from laboratory and pilot scale reactors for catalytic fast pyrolysis of woody biomass feedstock using microporous (H)-ZSM-5 zeolites. Unless mentioned otherwise, the values are *wt. %* on feed basis.

Entry	Reactor	Condenser	Feedstock	Feed intake (kg/h)	Catalyst (Si/Al ratio)	LY (wt. %)	NCG (wt. %)	SY (wt. %)	H ₂ O (wt. %)	CO (wt. %)	CO ₂ (wt. %)	Remarks	Ref./ Year
1	BFB (in situ)	Two condensers + ESP	Hybrid poplar wood	2	H-ZSM-5	34.2	51.6	Char: 14.2	8.59 (on liquid basis)	-	-	-	[101] 2010
2	BFB (in situ)	Chilled water condensers + ESP + coalescing filter	Hybrid poplar wood	0.1	H-ZSM-5	33.6	53.6	Char: 12.6	12 to 15.5 (on liquid basis)	CO/CO ₂ = 3.5 to 4.4		-	[76] 2010
3	BFB (in situ)	Two ethylene glycol condensers (-8 °C) + ESP	Hybrid poplar wood	-	ZSM-5 (7.78)	23.9 to 26.8	30.9 to 35.2	18.3 to 18.7	22.5 to 23.7	46.7 (on NCG basis)	35.5 to 37.3 (on NCG basis)	For vapour residence time of 6.5 s	[102] 2012
4	BFB (in situ)	Two ethylene glycol condensers (-8 °C) + ESP	Hybrid poplar wood	0.25	ZSM-5 (3.03)	~26.0	~29.0	~16.0	~23.0	13.6	10.5	-	[103] 2014
5	BFB (in situ)	Water cooled condenser + two glycol alcohol condensers (-5 °C)	Pine wood	0.02	H-ZSM-5 (23)	15.1	49.5	Char: 10.4, coke: 11.2	13.9	-	-	-	[104] 2008
6	BFB (in situ)	Three condensers in ice bath + four condensers in dry ice/acetone bath (-55 °C)	Pine wood	0.06	ZSM-5	-	-	Coke: 26.7	-	32.2	9.5	For T=600 °C and WHSV=0.35 h ⁻¹	[105] 2012
7	BFB (in situ)	ESP + dry ice cooled condensers	Mixed wood	0.12	ZSM-5	11.6	25.2	23.4	24.8	-	-	For the catalyst-to-biomass ratio=1.2	[106] 2013

Table 2.2. continued

Entry	Reactor	Condenser	Feedstock	Feed intake (kg/h)	Catalyst (Si/Al ratio)	LY (wt. %)	NCG (wt. %)	SY (wt. %)	H ₂ O (wt. %)	CO (wt. %)	CO ₂ (wt. %)	Remarks	Ref./ Year
8	BFB (in situ)	Water cooled condenser (20 °C) + ESP + glycol cooled condenser (-5 °C)	European spruce	0.7-0.8	ZSM-5 (140)	49.0	15.0	14.0	14.0	8.4	5.3	For WHSV=4.3	[86] 2013
9	BFB (in situ)*	A bubbler (0 °C) + two condensers in ice bath + six condensers in dry ice/acetone bath (-55 °C)	Pine wood	2 (slpm)	ZSM-5	-	-	Coke: 31.2	-	23.4	7.2	For WHSV=0.3, catalyst-to-biomass ratio=6	[98] 2014
10	CFB (in situ)*	Heat exchanger (230 °C/s) + stabilizer column (-30 °C)	Lignocel HBS (beech wood originated)	0.33	ZSM-5 based FCC (10 wt.% USY)	44.4	13.9	Char: 18.4	26.1	4.8	7.9	For solid heat carrier/biomass ratio=4.3	[32] 2002
11	AS (in situ)*	Water cooled steel tower and glass condenser + two ethylene glycol cooled glass condensers (-25 °C)	Pine wood	0.2	ZSM-5 based FCC	16.3	26.2	Char: 13.6, coke: 9.7	34	16.1	6.8	-	[100] 2013
12	CSB (in situ)	Two water cooled coils + ice trap	Pine wood	0.12-0.36	H-ZSM-5 (24)	59.7 (including water)	30.1	Char: 10.3	-	1.94	12.23	For T=450 °C	[99] 2000

Table 2.2. continued

Entry	Reactor	Condenser	Feedstock	Feed intake (kg/h)	Catalyst (Si/Al ratio)	LY (wt. %)	NCG (wt. %)	SY (wt. %)	H ₂ O (wt. %)	CO (wt. %)	CO ₂ (wt. %)	Remarks	Ref./ Year
13	BFB+PB (ex situ)	Dry ice/acetone condensers	Wood mixture	0.22-0.23	ZSM-5	Oil: 5.1, Aqueous organics: 4.1	31.8	Char: 16.3, coke: 11.4	30.1	15	10.6	T _{ex situ} =500 °C	[107] 1994
14	BFB+PB (ex situ)	Dry ice/acetone condensers	Wood mixture	0.22-0.23	ZSM-5 (50)	Oil: 5.7, Aqueous organics: 16.2	30.6	Char: 17.1, coke: 11.4	-	15	10.6	T _{ex situ} =500 °C	[108] 1995
15	AS+MB (ex situ)*	Water cooled steel tower and glass condenser + two ethylene glycol cooled glass condensers (-25 °C)	Pine wood	0.2	ZSM-5 based FCC	16.7	23.9	Char: 15.7, coke: 10.1	34.2	14.4	6.2	-	[100] 2013

* Continuous processes. Unless indicated otherwise, wt.%'s are expressed on feed basis. LY: liquid yield (organic fraction), NCG: non-condensable gas yield, SY: solid yield, BFB: bubbling fluidized bed, CFB: circulating fluidized bed, CSB: conical spouted bed, AS: auger screw, PB: packed bed, MB: moving bed (co-current flow). The sum of LY+NCG+SY+H₂O represents the mass balance closure.

As stated previously, the product distribution in CFP of biomass and the quality of the CFP-oil are likely dependent on the type and the properties of the catalyst, the operating conditions, the reactor technology, and liquid collection system (*i.e.* condenser). A comparison of results obtained from different studies (such as in Table 2.2) could be misleading due to the differences in the applied process conditions and the scales at which such data have been obtained. Such a comparison may end up in an apple-and-pear comparison. At the end, process reliability, and the price and quality of the CFP-oil will be decisive for the success of a technology developer.

2.2.3.3 Analytical reactors for CFP of biomass

Analytical pyrolysis, with a micro pyrolyzer directly connected to a GC/MS system (py-GC/MS), is a well-established technique to screen various catalyst/biomass combinations by performing simultaneous separation and identification of produced compounds in the GC-detectable vapour range. This helps to identify some of the main reactions that occur during CFP and to understand how the catalysts behave on a molecular basis leading to the production of desirable hydrocarbons and other chemicals. In this way, promising catalyst/biomass candidates can be identified and selected for larger scale experimentation [109,110]. Various biomass feedstock materials and model biomass compounds (*e.g.* cellulose, glucose, xylan, furan, *etc.*) have been tested batchwise by analytical pyrolysis, *viz.* in packed bed and tubular quartz micro reactors (see Tables A.2.1 and A.2.2 in the Supporting Information). The results show promising yields and selectivity for target compounds even though the absolute quantification of pyrolysis products have been less commonly applied. Besides, mass balance closure appears usually impossible. These types of reactors are not the real representatives of industrial/commercial scale reactors because they cannot be scaled up [92]. They are designed specifically for laboratory experiments. The differences in product yields and distribution between analytical and large scale reactor configurations were attributed to the difference in heat and mass transfer [92] which are not limiting in py-GC/MS. Hence, the results obtained from py-GC/MS systems are likely incomparable with the real bio-oil samples that are collected from the condensers of larger scale units (for detailed information and comparison see Chapter 4 in this thesis).

2.2.4 The choice of a suitable catalyst for CFP of biomass

The selection of appropriate catalysts for catalytic fast pyrolysis is one of the key factors affecting the outcome of the process. Apart from any cost considerations, a successful catalyst is characterized by three factors: activity, referring to the rate of reaction; selectivity, defined as the percentage of the spent reactant that forms the desired product; and stability, which is determined by how quickly the catalytic activity declines and determines how often the catalyst has to be replaced [74]. In CFP of biomass, an ideal catalyst should produce high yields of liquid product with a reduced oxygen content (by favouring CO, CO₂ and H₂O production), suppress the formation of coke, and minimize the amount of undesirable compounds present in the product oil (*e.g.* ketones, acids, polyaromatics). The latter are known to be detrimental for the direct use or further co-processing of bio-oil [72]. Moreover, the catalysts need to be both mechanically and thermally stable (resistance to deactivation)

and robust (the behaviour of the catalyst upon successive regeneration cycles) to improve overall lifetimes. To evaluate the catalytic activity and/or to compare different catalysts, turnover frequency (TOF), defined as the number of molecules that react per active site per unit time (in units of reciprocal time), can be used [74].

In large scale commercial CFP processes, all the details of catalyst performance, deactivation modes, and regeneration protocols must be carefully defined. Increasing the catalytic conversion by improving of the solid/vapour interface chemistry will be the key for catalyst improvements. By using a combination of computational and experimental techniques, rational design and development of catalysts can be accomplished [71].

2.3 Review on catalysis for catalytic fast pyrolysis of biomass

2.3.1 The role of catalysis in CFP of biomass

In the petrochemical industry, heterogeneous catalysis is widely used for the conversion of heavy oil fractions into lighter fuels and chemicals. Heterogeneous catalysts are those where the catalyst and the reactants are in different phases, most usually a solid catalyst and gas phase reactants. This phase difference between the two allows the gaseous reactants to react on the large surface area of the porous solid catalyst and be easily separated from each other afterwards [74]. In the last decades, improving the quality of bio-oil using heterogeneous catalysis has received considerable attention and a similar approach is carried over to biomass fast pyrolysis where the heavy oxygenated volatiles from the decomposition of biomass are deoxygenated and converted to lighter compounds when in contact with a suitable heterogeneous catalyst [72,111]. The challenges in developing this technology involve the development/optimization of advanced porous materials as efficient mono- and bi-functional catalysts for the production of high-grade bio-oils from biomass. To this end, cracking catalysts from different classes can be used in CFP research.

2.3.2 Catalysis used in CFP of biomass

Existing CFP research spans a wide range of catalyst and feedstock combinations tested over a range of temperatures and with various process parameters in an effort to develop fundamental knowledge on the effects of the catalysts. As candidate catalysts for CFP of biomass, micro- and meso-porous acidic zeolites, mesoporous materials with uniform pore size distribution, microporous/mesoporous hybrid materials doped with noble and transition metals, basic (metal oxides), and metal catalysts have been investigated in the literature.

2.3.2.1 Microporous acidic zeolites

Of the various catalysts studied in CFP of biomass to date, zeolite-based catalysts are the most tested ones. This interest is due to their vast availability, relatively low cost, and facile tunability with respect to its acidity. Zeolites are shown to be effective in promoting cracking and selective deoxygenation of pyrolytic vapours, resulting in the formation of aromatics and increasing the C/O ratio [46,109] while keeping the C/H ratio at an acceptable level. In general, zeolites are crystalline aluminosilicates (with trace metal ions) with three-dimensional porous structures. They have various elemental compositions and exhibit catalytic activity in up to 50% of their volume [73,112]. SiO_4 and AlO_4 are the primary building units of zeolites. They are linked by a common oxygen atom, forming a network of well-structured interconnected cavities and channels of molecular dimensions (Fig. 2.4). Due to the balance of anionic charge between the SiO_4 and AlO_4 units, zeolites have high active site densities [40]. The presence of acid sites in zeolites is of great importance for their catalytic activity. Generally two types of acid sites exist. Brønsted sites occur when the oxygen atom between Si and Al in the framework is protonated, resulting in a hydroxyl group [113]. In Fig. 2.2 it is shown how Brønsted acid sites exert their catalytic activity in the transformation of an oxygenated functional group into aromatics. Lewis acid sites are formed when the catalyst is dehydroxylated and dealuminated. They consist of extra-framework Al-species and are able to accept electrons. Fig. 2.3 shows a dehydroxylated zeolite with a Lewis acid site [114].

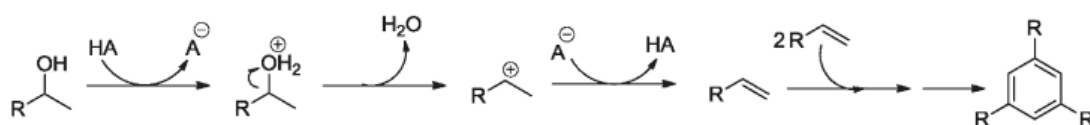


Fig. 2.2. Example of aromatics formation out of an oxygenated pyrolysis compound catalysed by Brønsted acid sites (HA) in zeolites [115].

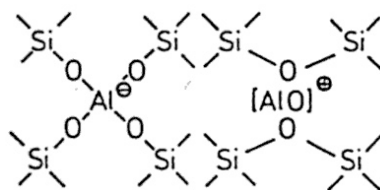


Fig. 2.3. Molecular structure of a dehydroxylated zeolite with AlO^+ as Lewis acid site [114].

To achieve the desired reaction selectivity, the strength distribution and the density of these acid sites can be controlled [24]. Since the reaction selectivity depends on the size and architecture of the pores, the pore sizes of zeolites (*ca.* 2-10 Å) make them suitable in terms of their shape selectivity [116].

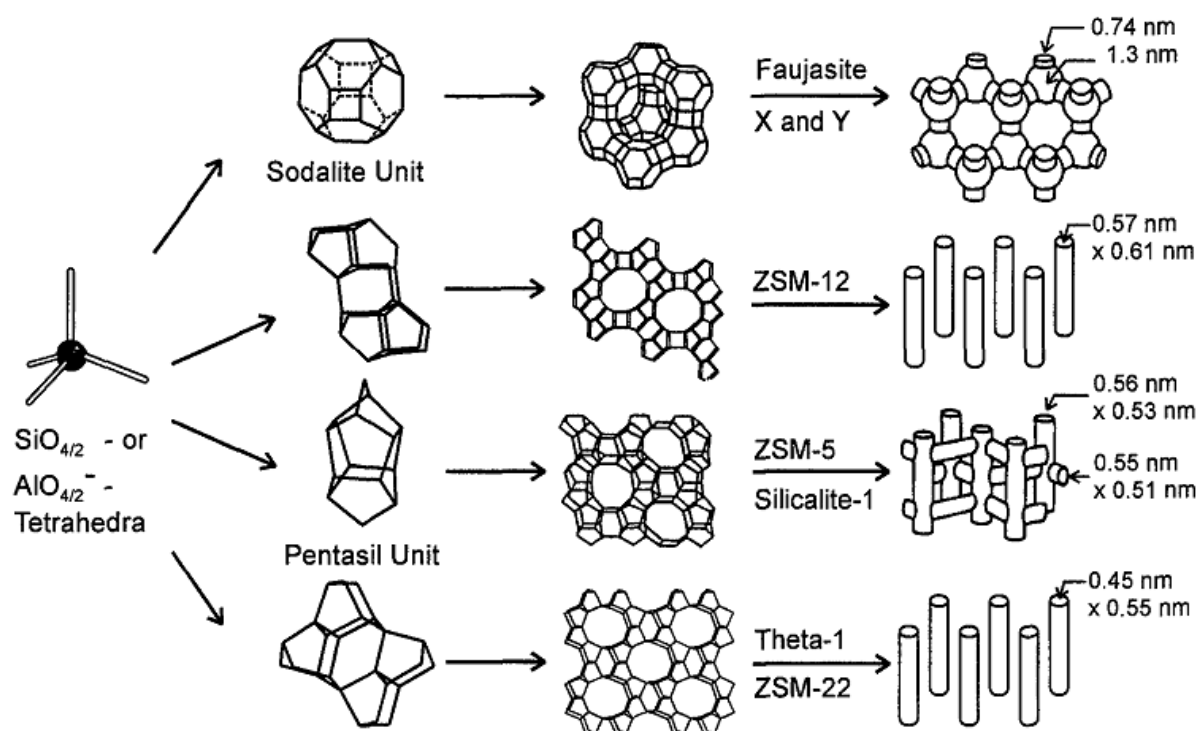


Fig. 2.4. Structures of four selected zeolites and their micropore systems and dimensions. Scheme was taken from [116]. Pore entrance size is given in nanometers (nm). (1 nm = 10 Å).

Several physical and chemical properties of heterogeneous catalysts, such as; structure, particle size, pore size (*i.e.* porosity, shape selectivity), acidity (*i.e.* nature of the active sites, *viz.* Brønsted and Lewis), mesoporosity, surface area, and metal-support interactions have been reported in CFP literature as the factors which significantly affect the reaction pathway and product selectivity [63]. The roles of these physical and chemical properties on the catalytic chemistry must be well understood if improved catalysts are to be designed for biomass conversion. Since this subject is out of the scope of this review, readers are directed to the review of Jens Weitkamp [116].

2.3.2.1.1 Reaction mechanism of CFP of biomass over microporous acidic zeolites

CFP of biomass is composed of two steps: *i)* rapid heating of biomass particles resulting in the formation of volatile organics in vapour phase (*i.e.* primary pyrolysis vapours), non-condensable gases (mainly CO, CO₂, H₂, and CH₄), and char, *ii)* the interactions between the released volatile organic vapours and the catalyst leading to catalytic conversion reactions. The vapour-catalyst interactions include oxygenates entering the pores of the catalyst where they are reformed to deoxygenated compounds.

A proper understanding of the detailed reaction mechanisms and kinetics is important for the design of catalysts. Although the reaction mechanism of catalytic conversion of biomass via CFP is not fully understood, there is evidence of some general reaction steps. As an example, the reaction chemistry for the production of aromatics and olefins from woody biomass via CFP using an acidic zeolite is shown in Fig. 2.5. In this scheme, cellulose is thermally decomposed (or pyrolysed) via dehydration reactions occurring under high temperatures and high heating rates to form smaller primary pyrolysis products such as anhydrosugars and other condensable oxygenated products (*i.e.* dihydroxyacetone, glyceraldehyde). The anhydrosugars then undergo dehydration and re-arrangement reactions to form intermediate oxygenates, *viz.* furanic compounds (*i.e.* furans, 2-methylfuran, furfural, furfuryl alcohol), smaller aldehydes, and H₂O. Such decomposition reactions occur either homogeneously or on the catalyst via acid catalysed dehydration, decarbonylation and decarboxylation. Hemicellulose also contributes to the formation of furanic compounds by thermal dehydration. These dehydrated species then diffuse into the zeolite pores where they undergo a series of acid-catalysed oligomerization, decarbonylation, decarboxylation, and dehydration reactions to form C₂-C₄ olefins, monocyclic aromatics, C₅ compounds, CO, CO₂, H₂O, and coke at the active sites. Isotope studies of CFP for ¹²C and ¹³C glucose have shown that oxygenates are all mono-isotopic and the produced aromatics are a random mixture of ¹²C and ¹³C [117]. This reveals that the monocyclic aromatic hydrocarbons (MAHs) are produced from a 'hydrocarbon pool' of decomposed oxygenated compounds. The lignin fraction of the biomass primarily forms monomeric compounds (*i.e.* phenols), as well as coke and CO₂ through free radical chemistry. Produced phenols then undergo acid-catalysed dehydration (H₂O production), decarbonylation (CO production), and decarboxylation (CO₂ production) reactions to form mono aromatic hydrocarbons. In the case of decarbonylation, a single carbon atom is consumed to remove a single oxygen atom. Obviously, the removal of oxygen in the form of CO₂ would be the preferable route. Oxygen removal via dehydration is in turn less desirable than CO₂ or CO formation because the highly energetic carbon-hydrogen bonds in the bio-oil should be preserved for the catalysed hydrocarbon forming reactions [100]. Coke formation is the major reaction competing with the production of target compounds (*i.e.* olefins and aromatics) and must be minimized. It can be formed both in the vapour phase and on the catalyst (*i.e.* polymerization). Moreover, coke reversibly deactivates the active sites of the catalyst by pore blockage and shielding the active sites; this results in the loss of catalytic activity. Polycyclic aromatic hydrocarbons (PAHs) (*e.g.* naphthalene) are formed in a second series of reactions of MAHs with other oxygenates, via acid catalysed polymerization reactions. The production of PAHs is undesirable and must be minimized. They are potentially carcinogenic [43] and cause a decrease in the yield of MAHs [45,85,92,105,118,119].

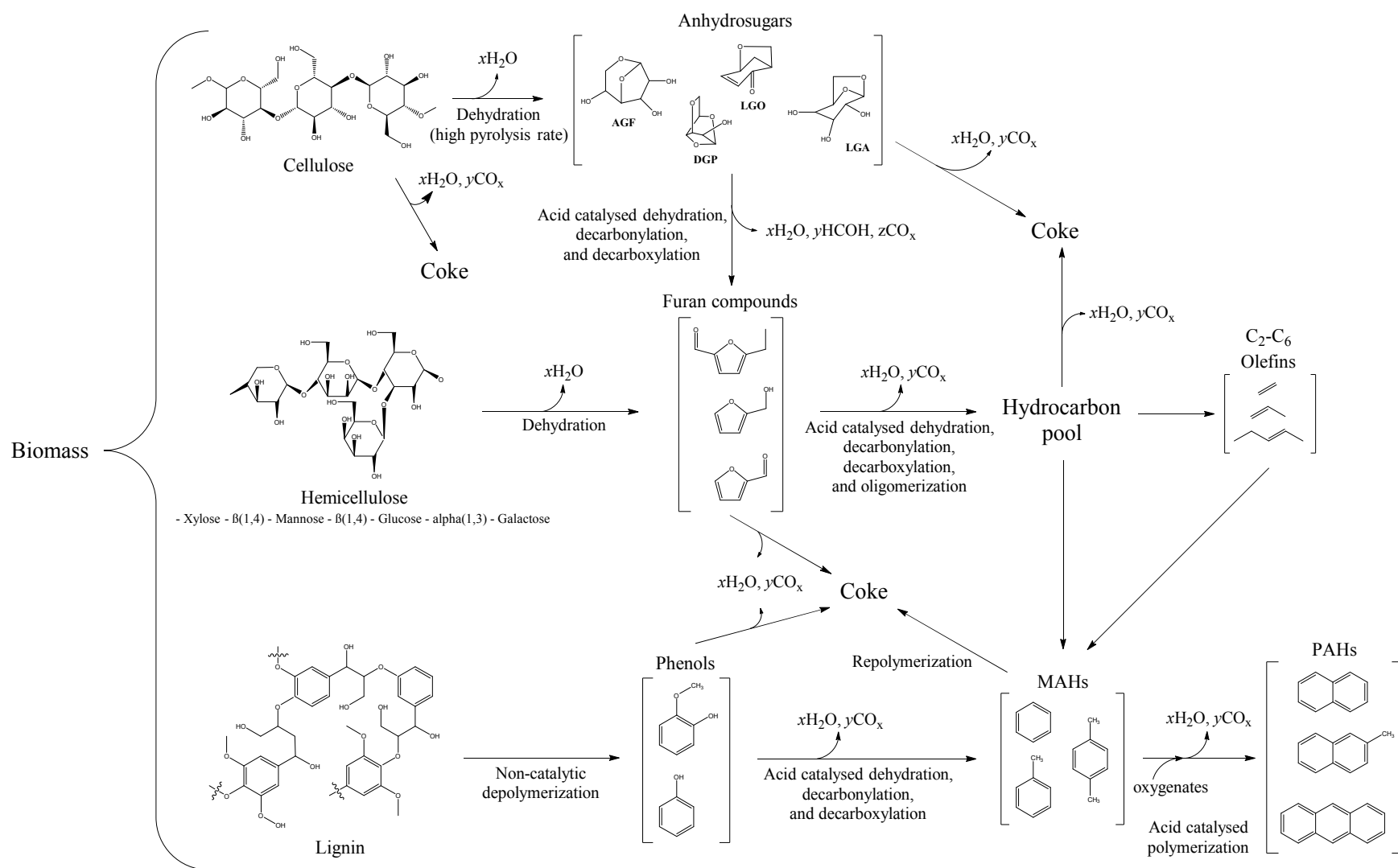


Fig. 2.5. Reaction chemistry for the catalytic fast pyrolysis of biomass on solid acid catalyst. Scheme constructed from previously published suggestions [41,75,87,92,120]. AGF: 1,6-Anhydro- β -D-glucofuranose; DGP: 1,4:3,6-dianhydro- α -D-glucopyranose; LGO: levoglucosenone; LGA: levoglucosan; MAHs: mono-aromatic hydrocarbons; PAHs: poly-aromatic hydrocarbons.

The yield of useful petrochemical products (*i.e.* olefins, monoaromatics) and coke is a function of the effective hydrogen-to-carbon ratio (H/C_{eff}) [121] of the biomass feedstock. It is defined in Eq. 2.1, where H, C, and O are the moles of hydrogen, carbon, and oxygen present in the feed, respectively:

$$H/C_{\text{eff}} = (H - 2O)/C \quad \text{Eq. 2.1}$$

This ratio can be used to give an indication of whether a certain biomass feedstock (or a mixture of biomass and liquid hydrocarbons) can be upgraded easily using zeolite catalysis. The H/C_{eff} ratio of biomass ranges from 0 to 0.3, whereas that of petroleum-derived products is from 1 (for benzene) to slightly over 2 (for liquid alkanes) which reveal that biomass is a hydrogen-deficient feedstock. Feedstock with an H/C_{eff} ratio of less than 1 would be difficult to upgrade over a zeolite catalyst due to a rapid deactivation of the catalyst [122]. Co-feeding of particular hydrocarbons like methanol, 1-propanol, 1-butanol, 2-butanol, *etc.* together with the biomass can improve the hydrocarbon pool and increase the overall H/C_{eff} ratio. This would favour the petrochemical (aliphatic and/or aromatic hydrocarbons, olefins) yield from CFP of biomass [85,105].

2.3.2.1.2 CFP research based on microporous acidic zeolites

A variety of microporous zeolites have been tested, such as ZSM-5, FCC, Y- and β -zeolites, mordenite, ferrierite, SAPO (silicoaluminophosphate), USY, *etc.* Microporous acidic zeolites can also be modified by incorporation of metals as promoters (*e.g.* Ga/ZSM-5, FeCrCu/FCC, Re-USY, Co/HZSM-5, Fe/H- β , Ga/H-Y). The literature dealing with the utilization of microporous zeolites (both mono- and bi-functional) for CFP of woody biomass as feedstock at varying process conditions is summarized in Tables A.2.3 (in situ studies) and A.2.4 (ex situ studies) in the Supporting Information.

ZSM-5 has been used more than any other microporous zeolite because it shows the best overall performance in terms of thermal stability, deoxygenation capability and the production of aromatic hydrocarbons [47,62]. Agblevor *et al.* [101] (entry no.1 in Table A.2.3, entry no.1 in Table 2.2) tested the performance of H-ZSM-5 catalyst in a bubbling fluidized bed reactor (in situ) at 450 °C and obtained 34.2 wt.% liquid, 51.6 wt.% of gas, and 14.2 wt.% of combined char and coke yields. Compared to the non-catalytic bio-oil produced in the same set-up under identical process conditions, catalytic oils were more stable, less acidic (total acid number, TAN decreased from 90 to 41), exhibited insignificant aging over 10 months, had low viscosity, contained mainly creosols and methyl-substituted phenols.

A crucial parameter in the development of catalysts for CFP is the pore size of the catalyst because it can limit the catalytic selectivity. In case of medium pore zeolites (*i.e.* ZSM-5, ZSM-11), large-molecular oxygenates cannot enter the pores and could polymerize to form coke on the catalyst surface. That would decrease the hydrocarbon yield and cause a rapid deactivation. On the other hand, mesoporous and macroporous catalysts can crack large molecules but cannot convert them into desired chemicals (*i.e.* aromatics, olefins) [123]. In another study of Agblevor *et al.* [76] (entry no.2 in Table A.2.3, entry no.2 in Table 2.2), it was observed that the pore size of the catalyst played a critical role in catalytic pyrolysis. Lignin derived intermediate products (radicals, ions, and unstable molecules) larger than the

pore size of the catalyst could not diffuse to the active sites of HZSM-5 catalyst and were therefore not cracked into gaseous products. However, the carbohydrate derived intermediates smaller than the pore size of the catalyst were converted into gaseous products such as carbon dioxide, carbon monoxide, and C₁-C₄ hydrocarbons.

Atutxa *et al.* [124] (entry no.35 in Table A.2.3) studied the effect of H-ZSM-5 zeolite on the in situ pyrolysis of pine wood at 400 °C. They proposed a kinetic model that combines thermal pyrolysis with the subsequent catalytic transformation of the products obtained in the first step in a conical spouted bed reactor. The study examined how the amount of catalyst, *i.e.* different amounts of acid sites in the bed material of the reactor, affected the yields of the various product phases and their chemical composition. It was found that higher catalyst-to-feed ratios increased the gas yield (mainly CO and CO₂), whereas the total liquid yield decreased notably. The decrease in the liquid yield was attributed to the transformation of 'heavy liquid' to 'light' liquid and gases. The char yield was fairly constant for each catalytic experiment but lower than the non-catalytic one. The CO/CO₂ ratio increased with increasing catalyst mass. Overall, the bio-oil obtained through the catalytic pyrolysis of pine wood with H-ZSM-5 was less oxygenated than the non-catalytic bio-oil. However, the light fraction was more severely deoxygenated than the heavy fraction, which is an indication of the higher global reactivity towards the compounds in the light fraction, especially of alcohols and acetic acid. Kinetic constants for the developed kinetic model were also reported.

Olazar *et al.* [99] (entry no.34 in Table A.2.3, entry no.12 in Table 2.2) studied catalytic pyrolysis of pine wood over H-ZSM-5 catalyst in a conical spouted bed reactor at 400, 450, and 500 °C. The utilization of catalyst increased the gas yield, which was accompanied by decreases in the yields of liquid and char. They reported 30.8 wt.% total organic yield (12% carbon yield for aromatics) at 450 °C. Partial deoxygenation of the produced bio-oil was achieved and reported as higher water content. Compared to the non-catalytic pyrolysis, CO₂ production decreased and CO production increased. H-ZSM-5 was found to be efficient for the production of light hydrocarbons (C₄) and aromatics.

Of the previously mentioned catalyst properties, the acidity of the catalyst plays the most crucial role in the upgrading reactions. Aho *et al.* [125] (entry no.7 in Table A.2.3) used the proton form of beta zeolite (H-Beta) as a catalyst for the pyrolysis of pine wood in a bubbling fluidized bed reactor at 450 °C, and investigated the influence of the catalyst acidity on the yields of pyrolysis products and on the properties of the bio-oil formed. As an indicator of catalyst acidity, varying silica-to-alumina ratios (*i.e.* Si/Al ratio, SAR) of 25, 150, and 300 were tested. Overall, the organic oil yield decreased in the presence of catalysts. It was observed that with the increase in the acidity (decrease in the Si/Al ratio), catalysts tend to form less organic oil, and respectively more gas, coke, water and PAHs.

The chemical composition of bio-oil depends also on the structure of the acidic zeolite catalysts. Aho *et al.* [104] (entry no.8 in Table A.2.3, entry no.5 in Table 2.2) examined the influence of different structures of microporous acidic zeolites in proton forms such as H-Beta, H-Y, H-ZSM-5, H-MOR (*i.e.* H-mordenite) via catalytic pyrolysis of pine wood in a bubbling fluidized bed reactor at 450 °C. In the presence of both zeolites, a decrease in the organic fraction of the liquid product was observed. Out of the four different zeolites tested

under identical process conditions H-ZSM-5 gave the highest liquid yield and exhibited lower selectivity to acids and alcohols and higher selectivity to ketones. H-MOR was found to be effective for minimizing the formation of PAHs and yielded smaller quantities of PAHs than the other zeolites tested. The nature of the coke formed on different zeolites was also studied by dissolving the zeolite in hydrofluoric acid and then dissolving the coke in dichloromethane. Among the four zeolites, H-Y zeolite had the highest coke content (H-Y>H-Beta>H-MOR>H-ZSM-5). This was attributed to its highest initial surface area and large cavities in the structure of H-Y allowing larger molecules to diffuse into the pores of the catalyst.

Samolada *et al.* [69] (entry no.29 in Table A.2.3, entry no.15 in Table A.2.4, entries no.3 and no.12 in Table A.2.5, entries no.16 and no.24 in Table A.2.6) studied a range of catalysts (microporous, mesoporous and transition metals) in the catalytic pyrolysis of beech wood (Lignocel HBS 150-500) in a packed bed reactor and showed that H-ZSM-5 was a more suitable catalyst for aromatics production than the other ones. H-ZSM-5 completely removed water and oxygen from the organic liquid and converted undesirable carbonyls to hydrocarbons at the applied conditions (see Table A.2.3) but caused a significant decrease in the organic liquid fraction and increase of water (via dehydration). This is not surprising as the catalysts promotes cracking reactions, leading to a decrease in the yield of organic liquid fraction due to the removal of oxygen. Besides, all the catalysts were found to increase gas production at the expense of liquid generation.

In CFP literature, various types of metals (*i.e.* Re, Ga, Fe, Na, Ni, Co, Pt, Mo, Cr, and Cu) have been incorporated mainly in FCC and ZSM-5 zeolites, converting them from being monofunctional to bifunctional catalysts, wherein the support itself acts as a catalyst as well. The use of metals controls the strength of the acid sites and promotes the deoxygenation required for the formation of hydrocarbons. It could enhance both, the production of higher-quality bio-oil and the selectivity for the production of MAHs [47]. Moreover, the bifunctional activity (acid and metal functions) reduces the formation of coke [126]. Cheng *et al.* [127] (entry no.13 in Table A.2.3) tested the gallium modified Ga/ZSM-5 in the catalytic pyrolysis of pine wood in a bubbling fluidized bed at 550 and 600 °C and found that the rate of aromatization increased with the modification of ZSM-5 with gallium. Ga seemed to increase the rate of decarbonylation and olefin aromatization, while ZSM-5 catalysed the remaining reactions for the production of aromatics (*e.g.* oligomerization and cracking).

To facilitate large scale production of refinery-ready intermediates, commercial FCC (fluid cracking catalyst) can be utilized in CFP of biomass. The acidic Y-zeolite is the primary active component in FCC and ZSM-5 is widely used as a supplement [102]. The bimodal pore size distribution, arising from the combination of microporous and mesoporous structures, is the reason for the effective behaviour of these catalysts. Compared to ZSM-5 catalysts, FCC produces less bio-oil and higher amounts of coke in CFP of biomass, due to its larger pore sizes (7.4 µm) and higher BET surface area. Obviously, the amount of FCC used within the process must be carefully controlled in order to optimise the yield of bio-oil versus its quality [40,82]. Lappas *et al.* [64] (entry no.10 in Table A.2.3) investigated the influence of temperature (450 and 500 °C) in non-catalytic (with silica sand) and catalytic fast pyrolysis of beech wood in the presence of a FCC catalyst (with a fixed catalyst-to-feed weight ratio equal

to 16) in a continuously operated circulating fluidized bed reactor. In the presence of FCC catalyst, bio-oil yield (water+organics) decreased from 74 wt.% to 46.5 wt.% at 500 °C. The catalytic bio-oils contain more hydrocarbons (*ca.* 2 wt.% on organic fraction) and less heavy oxygenated compounds (*ca.* 20 wt.% on organic fraction) compared with the non-catalytic bio-oil. Due to its high activity, FCC catalyst increased gas, water, and carbonaceous solids (coke and char) production at the expense of bio-oil. It was also found that FCC favoured decarbonylation and decarboxylation reactions which resulted in more CO and CO₂ production. With the temperature increase from 450 to 500 °C, CO yield increased from around 5 wt.% to about 10 wt.%.

In another work of Lappas *et al.* [32] (entry no.9 in Table A.2.3, entry no.10 in Table 2.2), the effect of a FCC catalyst and a ZSM-5 based FCC (10 wt.% USY) additive were investigated in catalytic pyrolysis of beech wood (Lignocel HBS 150-500) in a circulating fluidized bed reactor (continuous mode). The main observation was that in the presence of a catalyst, water, non-condensable gases (specifically CO and CO₂), coke on spent catalyst, and char increased. On the other hand, catalysts favoured the deoxygenation reactions and increased the quality and the composition of bio-oil remarkably. The effect of catalyst-to-biomass ratio was also studied and was concluded that it is an important parameter affecting the product yields and selectivity. It was reported that an increase in catalyst-to-feed ratio resulted in higher yields of water and gas, lower coke, and an organic fraction with less oxygenated compounds, more hydrocarbons and less heavy oxygenates. Stability tests (based on viscosity measurements) revealed that the stability of a bio-oil is not only a function of the concentration of some chemical groups (carbonyls) but also of the molecular weight of these groups. It was concluded that the stability of a bio-oil depends on the pyrolysis experimental conditions (temperature, catalyst-to-biomass ratio) and the catalyst type and activity.

Horne and Williams [128] (entry no.5 in Table A.2.4) studied the *ex situ* catalytic pyrolysis of wood waste over H-ZSM-5 in a dual zone bubbling fluidized bed reactor. Pyrolysis (primary) and packed bed reactors for catalytic vapour phase treatment were operated at 550 and 500 °C, respectively. The effect of catalyst dilution on the product yields was examined and found to be beneficial for the production of hydrocarbons. They reported that in case of *ex situ* treatment of pyrolysis vapours, oxygen removal takes place mainly as H₂O production at lower catalyst bed temperatures and as CO and CO₂ at higher bed temperatures. They observed a shift towards lower molecular weight species with increasing catalyst bed temperatures as well [107] (entry no.2 in Table A.2.4, entry no. 13 in Table 2.2). Detailed analysis of the upgraded bio-oil showed that, besides the production of economically valuable chemicals in high concentrations, the quantity of undesired PAHs was favoured with an increasing catalyst bed temperature [129] (entry no.3 in Table A.2.4).

In another study of Horne *et al.* [108] (entry no. 4 in Table A.2.4, entry no. 14 in Table 2.2) the same set-up was used to test ZSM-5 for pyrolysis vapours treatment in the presence of methanol. A controlled flow of methanol was added to the pyrolysis vapour stream just before the catalytic reactor. A catalyst-to-feed ratio (weight of the catalyst used/weight of the biomass fed) of 1.16 was used in the experiments. With the addition of methanol, a threefold increase in aromatic yield was reported compared to the non-catalytic pyrolysis. In all catalytic experiments, low organic liquid yields (*ca.* 5 wt.%) were reported. There was an

overall increase in the hydrocarbon products including alkylated phenols and aromatics. The alkylated compounds are thought to compete with the production of PAHs and which would explain the corresponding decrease in 3-, 4-, and 5-ring PAHs. Co-processing of pyrolysis vapours was also investigated; *viz.* by the injection of varying amounts of methanol. This increased the contents of water and alkylated hydrocarbons, and decreased CO and CO₂ yields. Li *et al.* [51] (entry no.6 in Table A.2.4) also studied the ex situ upgrading of sawdust originated pyrolysis vapours over an H-ZSM-5 zeolite in a bubbling fluidized bed reactor. At 500 °C and a WHSV of 3 h⁻¹, the liquid yield reached the maximum (*ca.* 46 wt.% on biomass basis) and a remarkable decrease in the compounds with high oxygen contents were observed. In comparison to the non-catalytic bio-oil, a decrease in the amounts of acids (from 14.5 to 3.0 wt.%) and an increase in the aromatics (from 0.5 to 16.8 wt.%) were observed in the presence of the catalyst.

Mihalcik *et al.* [109] (entry no.10 in Table A.2.4) tested five different zeolites (H-ZSM-5, H-Y, H-Beta, H-Mordenite, and H-Ferrierite) for the catalytic fast pyrolysis of various biomass feedstock including oak wood on a micro scale. The experiments were performed ex situ in a Py/GC-MS (Pyroprobe followed by a packed catalyst bed) with a catalyst-to-biomass ratio of 5. It was reported that, in terms of the production of aromatics, H-ZSM-5 was the most effective catalyst and the activity was in the following order: H-ZSM-5 > H-Beta > H-Mordenite > H-Ferrierite ~ H-Y. They also showed that with the increase of the catalyst acidity (decrease in Si/Al ratio), the deoxygenation of the vapours was favoured, a step in the reaction pathway to aromatic hydrocarbons.

Application of metal modified microporous acidic zeolites in the ex situ catalytic pyrolysis of woody biomass has also been reported. Park *et al.* [130] (entry no.7 in Table A.2.4) performed the ex situ catalytic upgrading of pyrolysis vapours over H-ZSM-5, H-Y and their gallium modified counterparts (*i.e.* Ga(1%)/H-ZSM-5, Ga(1%)/H-Y) in a packed bed reactor, installed in the upper part of a bubbling fluidized bed reactor operating at 475 °C. H-ZSM-5 was shown to be more effective in upgrading the bio-oil than H-Y; oxygen was mainly removed from the bio-oil by the increased production of H₂O, CO and CO₂. Under identical process conditions, the introduction of 1 wt.% Ga into ZSM-5 (*i.e.* Ga/ZSM-5) produced slightly more bio-oil (including water) than H-ZSM-5 and had better selectivity to detectable aromatic hydrocarbons; benzene derivatives like toluene and xylenes were increased. The reason for the increased selectivity towards benzene derivatives was explained by the positive impact of Ga on benzene alkylation. However, Ga/ZSM-5 resulted in a lower degree of deoxygenation compared to that of H-ZSM-5. This was explained as the decrease in the number of strong acid sites of H-ZSM-5 caused by the impregnation of Ga. In another study, Iliopoulou *et al.* [131] (entry no. 18 in Table A.2.4, entry no.14 in Table A.2.6) incorporated transition metals such as nickel and cobalt into ZSM-5 (1, 5, 10 wt.%). The presence of metal increased the production of aromatics derived from lignocellulosic biomass. This was attributed to the effect of these transition metals in promoting the dehydrogenation reactions.

Aho *et al.* [132] (entry no.1 in Table A.2.4) investigated the influence of β , Y, and ferrierite zeolites, as well as their iron modified counterparts (*i.e.* H-Fer, Fe-H-Fer, H-Y, Fe-H-Y, H- β , Fe-H- β) during the ex situ upgrading of pyrolysis vapours of pine wood in a dual-bubbling fluidized bed reactor at 450 °C. For all experiments, a fixed catalyst-to-feed ratio of 0.11 was used and the bio-oil yields ranged between 43.5 and 52.7 wt.% (including the water). It was suggested that the pore size of the zeolites played an important role in the activity for the deoxygenation of the pyrolysis vapours and in the formation of coke. β -zeolite, which has the largest pore size among the three zeolites, was found to be the most active in the deoxygenation reactions, followed by Y and ferrierite. On the other hand, ferrierite, which has the smallest pore size, resulted in the lowest amount of coke formation. Although iron modified zeolites had negligible effects on the deoxygenation, they formed more coke than the parent catalysts. In the presence of all catalysts, the cracking effect was observed as the decrease in the formation of levoglucosan. Iron modification on zeolites led to an increase of methyl-substituted phenols, a decrease in methoxy-substituted phenols and did not affect the CO/CO₂ ratio.

French and Czernik [59] (entry no.19 in Table A.2.4) tested forty different commercial and laboratory synthesized catalysts for their hydrocarbon production performance in CFP of lignocellulosic biomass using a tubular quartz micro-reactor coupled with a molecular beam mass spectrometer (MBMS). In accordance with the findings of Aho *et al.* [104], French and Czernik showed that ZSM-5 (parent and modified) resulted in better deoxygenation of lignocellulosic biomass than that of other tested large pore zeolites. Maximum hydrocarbon yields of 16 wt.% (incl. 3.5 wt.% toluene) were obtained with Ni, Co, Fe, and Ga modified ZSM-5 catalyst. It was concluded that the presence of transition metals would affect the mode of oxygen rejection by producing more CO_x and less H₂O, making in that way more hydrogen available for incorporation into hydrocarbons.

Section conclusion:

Microporous acidic zeolites, (H-)ZSM-5 in particular, are the most tested catalysts in CFP research. In general, they favour the production of less oxygenated, more stable and less acidic liquid products compared to non-catalytic bio-oil. Like most of the catalysts used in CFP of biomass, they promote cracking reactions, leading to a decrease in the yield of organic liquid fraction due to the removal of oxygen. However, the amount of light hydrocarbons (C₄) and aromatics increase, while the production of acids, sugars and PAHs is suppressed; this indicates the production of a liquid product with a better quality.

Some catalyst properties such as the pore size and the acidity (Si/Al ratio) affect the performance of microporous acidic zeolites. The pore size of the microporous acidic zeolites plays an important role in the activity for the deoxygenation of the pyrolysis vapours and in the formation of coke. Small pore sizes prevent the diffusion of large molecules (*i.e.* lignin derived intermediates; radicals, ions, and unstable molecules) to the active sites of microporous catalysts (particularly H-ZSM-5) and hence from being cracked to lighter products. On the other hand, the carbohydrate derived intermediates, which are often smaller than the pore size of the catalyst, are easily converted to gaseous products such as carbon dioxide, carbon monoxide, and C₁-C₄ hydrocarbons. Some microporous zeolites such as H-Y

and H-Beta allow larger molecules to diffuse into the pores of the catalyst due to their large pore entries and large cavities in their structure. However, this favours the formation of coke. Microporous acidic zeolites tend to form less organic oil with a reduced oxygen content, and more gas, coke, water and PAHs when their acidity is increased (decrease in the Si/Al ratio). The increase in catalyst-to-biomass ratio results in higher yields of water and gas, and a lower organic fraction containing less oxygen, more hydrocarbons, and less heavy oxygenates. The reason for the decrease in the liquid yield in this case is the formation of light liquid fraction and partially gases at the expense of the heavy liquid fraction. The incorporation of metals in microporous acidic zeolites affects the mode of oxygen rejection by producing more CO_x and less H₂O, making in that way more hydrogen available for incorporation into hydrocarbons. The presence of metals reduces the formation of coke as well.

2.3.2.2 CFP research based on mesoporous materials

In recent years, mesoporous materials, with pore sizes much larger than that of traditional microporous zeolites (*e.g.* 30 Å pores in Al-MCM-41 compared to *ca.* 5.5 Å for ZSM-5 [44]), have attracted great interest for their potential to convert the large molecules in the pyrolysis vapours, particularly lignin derived compounds. It is supposed that these molecules can enter easily, be reformulated, and exit the catalyst matrix with less chance of coke deposition and blocking of the pores. From the CFP literature, it appears that mesoporous materials (MCM-41, SBA-15, MSU, *etc.*) and their metal modified counterparts (*e.g.* Al-MCM-41, Cu-Al-MCM-41, Al-SBA-15) have been studied widely because of their high surface areas, large pore sizes (>2 nm) and moderate acidities. In general, these mesoporous catalysts are less active than microporous ZSM-5 under similar conditions. However, careful tuning of the acidity and the pore size of these catalysts could result in high product yields/selectivity [85,133]. The literature concerned with mesoporous materials (both mono- and bi-functional) for CFP of woody biomasses under different process conditions, is summarized in Table A.2.5 in the Supporting Information.

Among the mesoporous acidic materials, MCM-41 has received most attention in the CFP literature. MCM-41 materials possess high surface areas (>1000 m²·g⁻¹), moderate acidity, and a hexagonal array of uniform mesopores, the size of which can be tailored in the range of 1.4-10 nm [62]. Alumina incorporated into MCM-41 materials; namely Al-MCM-41 catalysts, showed promising deoxygenation capabilities, as well as selectivity for specific compounds (*i.e.* phenolics), although they typically have lower thermal stability and acidity than that of the microporous zeolites (*e.g.* ZSM-5). The nature of the acid sites in Al-MCM-41 (both Brønsted and Lewis acid sites are present) has a positive effect on the molecular distribution of the resulting bio-oils [134]. Iliopoulou *et al.* [133] (entry no.14 in Table A.2.5) studied the effects of acidity (different Si/Al ratios) and steam stability of Al-MCM-41 materials for the *ex situ* upgrading of pyrolysis vapours in a packed bed reactor operated at 500 °C. The results obtained were compared to those of MCM-41 and non-catalytic pyrolysis. They found that Al-MCM-41 materials with lower acidities (high Si/Al ratio) enhanced the production of the organic phase of the bio-oil and chemical composition of it (increase in phenols and reduction of corrosive acids) while higher acidities favoured the conversion of pyrolysis vapours toward gases and coke. Moderate steam reforming over Al-MCM-41

materials resulted in a reduction of their surface area and number of acid sites by 40-60%. However, the steamed samples were still active in upgrading of biomass pyrolysis vapours.

Antonakou *et al.* [135] (entry no.11 in Table A.2.5) examined three Al-MCM-41 materials with different acidities (Si/Al ratios of 20, 40, and 60), and three metal containing (Cu, Fe, and Zn) Al-MCM-41 samples as catalysts for the ex situ CFP of beech wood originated Lignocel HBS in a packed bed reactor operating at 500 °C. Lower Si/Al ratios and the consequent higher surface acidity of the catalysts were found to increase the production of phenolics, as well as the product yields. Adversely, less acidic Al-MCM-41 catalyst favoured the production of aromatics. All tested catalysts resulted in a decrease in the undesirable fractions of acids, carbonyls and heavy compounds. The incorporation of transition metals decreased the production of aromatic hydrocarbons and PAHs. This was attributed to a redox transformation of the bulky PAH molecules, forming smaller products from their decomposition. Al-MCM-41(20), Fe-Al-MCM-41 and Cu-Al-MCM-41 showed the best performance in terms of the production of phenols and phenolics. In addition to that, Cu-Al-MCM-41 caused the largest increase of H₂ in the gaseous product which is inhibitive for the production of hydrocarbons. In the same reactor and with identical process parameters, Triantafyllidis *et al.* [134] (entry no.13 in Table A.2.5, entry no. 16 in Table A.2.4) performed the ex situ upgrading of pyrolysis vapours using two mesoporous aluminosilicate materials (MSU-S/H_{BEA}, MSU-S/W_{BEA}) assembled from zeolite beta seeds, and compared their performances with that of Al-MCM-41. The MSU-S catalysts led to high coke yields and significantly reduced the organic phase of the bio-oil compared with non-catalytic pyrolysis and with the Al-MCM-41. The MSU-S materials showed high selectivity towards aromatics, heavy fractions, coke and PAHs, which was attributed to stronger acid sites than those of Al-MCM-41. However, MSU-S materials produced negligible amounts of acids, alcohols, carbonyls, and very few phenols. This work revealed that the activity and the product selectivity of MSU-S materials are insufficient for their use in catalytic biomass pyrolysis.

Adam *et al.* [136] (entry no.7 in Table A.2.5) studied the ex situ pyrolysis of spruce wood in a Py-GC/MS system in the presence of four different Al-MCM-41 catalysts modified by pore enlargement and the incorporation with copper into the structure (*i.e.* Al-MCM-41 (20), MCM-41 with spacer, MCM-41 with C₁₈, Cu-Al-MCM-41). In the presence of all catalysts, the yield of furans and acetic acid increased while the yield of high molecular mass phenols (syringyl and guaiacyl) decreased. Levoglucosan, one of the main pyrolysis products of cellulose, was completely eliminated while a slight increase in the hydrocarbon yields was observed. All catalysts favoured the removal of water from hydroxyl group containing molecules. Pore enlargement and the incorporation of copper reduced the contents of acetic acid and water in bio-oil and the production of higher molecular mass products was favoured.

Samolada *et al.* [69] (entry no.3 in Table A.2.5) reported that Al-MCM-41 catalyst effectively removed the acids from the bio-oil. However, this catalyst exhibited poor hydrothermal stability (leading to dealumination) as compared to ZSM-5, suggesting that further upgrading of this material is needed for the CFP process. In order to resolve the related drawbacks, catalysts containing both the beneficial properties of zeolites and mesoporous catalysts must be developed. Lee *et al.* [137] (entry no.6 in Table A.2.5) synthesized mesoporous materials from zeolites (MMZs) using commercially available beta and ZSM-5

zeolites. They used them for ex situ CFP of woody biomass in a fluidized bed reactor. The MMZs (*i.e.* Meso-Beta and Meso-ZSM-5) were found to be promising catalysts for CFP because they showed excellent activity, stability and selectivity for the desired formation of phenolics and reduction of oxygenates if compared with Al-MCM-41. Park *et al.* [138] (entry no. 10 in Table A.2.5) synthesized a mesoporous mordenite framework inverted (MFI) zeolite and compared its activity with H-ZSM-5 and MMZ_{ZSM-5} for the ex situ catalytic pyrolysis of radiate pine in a packed bed reactor operating at 500 °C. The mesoporous MFI zeolite exhibited the highest activity in terms of deoxygenation and aromatization. Although the yield of organic fraction of bio-oil decreased with MFI, this zeolite showed pronounced selectivity for highly valuable aromatics (BTX). The incorporation of gallium into the MFI zeolite (Ga-MFI) favoured the yield of the organic fraction and increased the resistance to coke deposition.

SBA-15 is known to have long-range order, large mono-dispersed mesopores, thick walls (typically between 3 and 9 nm), adjustable pore size from 5 to 30 nm, and a higher hydrothermal and thermal stability than MCM-41 type materials [68,72]. Lu *et al.* [139] (entry no.8 in Table A.2.5) tested parent and aluminium modified Al-SBA-15 catalysts with different acidities (Si/Al ratios of 10, 20, 35, and 70) in a Py-GC/MS system at 500 °C with a fixed catalyst-to-feed ratio of 1. All Al-SBA-15 materials were found to be more active than the siliceous SBA-15. With decreasing Si/Al ratio, the cracking effects of the catalysts were enhanced. In the presence of SBA-15 catalysts, the yields of heavy furans, light phenols, and light carbonyls and ketones decreased, while those of light furans, furfural, light phenols and acetic acid increased.

Section conclusion:

Mesoporous materials offer large pore sizes and high surface areas. These unique properties allow the conversion of large molecules (*e.g.* lignin derived compounds) and suppress the formation of coke. Mesoporous materials with lower acidities (high Si/Al ratio) found to enhance the yield of CFP-oil and the phenolic and aromatic compounds in it. Incorporation of metals to mesoporous materials, in general, results in a decrease in the production of aromatics, PAHs, acids and the water in CFP-oil. Further optimization is required to resolve the problem of poor hydrothermal stability of these catalysts.

2.3.2.3 CFP research based on basic (metal oxides) and metal catalysts

The synthesis of basic zeolites from their reaction with ammonia at elevated temperatures provides unique activity and selectivity for base-catalysed reactions [140]. Base catalytic activity has been shown to lead to much higher conversions compared to acid catalysts in other reactions resulting in biofuel compounds, such as aldol condensation and transesterification [141]. Moreover, transition metal oxide based catalysts (*e.g.* ZnO [142], CoMo and NiMo [143]) have been used for the production of liquid fuels from biomass via CFP. The literature regarding the utilization of basic catalysts (metal oxides) are summarized in Table A.2.6 in the Supporting Information.

Nokkosmaki *et al.* [142] (entries no.8 and 9 in Table A.2.6) studied the influence of three different zinc oxide catalysts (*i.e.* ZnO, ZnO (0.5% Mg), ZnO (15% alumina)) to investigate their effects on the composition and on the stability of the bio-oil. The pyrolysis vapours of pine wood were passed through a fixed bed of catalyst operating at 600 °C (*ex situ*). The stability of the oils was determined by measuring the change in viscosity; it was determined by thermally treating (ageing) the oil and comparing the viscosity and water content of it before and after the treatment. The major finding of this work was that the use of ZnO significantly lowered the viscosity of the catalytically produced oil if compared with the non-catalytic oil. Besides, the increase in viscosity after storage at elevated temperatures was also lower for the catalytically produced oil. However, ZnO was found to be just a mild catalyst causing only a small reduction in the liquid yield with only a 2 *wt.%* increase in gases (in comparison to the non-catalytic case). Moreover, at increasing catalyst temperature (from 300 °C to 400 and 500 °C), the formation of anhydrosugars and formic acid was reduced.

Lu *et al.* [144] (entry no.11 in Table A.2.6) observed different capabilities of various metal oxides (*i.e.* MgO, CaO, TiO₂, Fe₂O₃, NiO, and ZnO) in the *ex situ* upgrading of poplar wood vapours in a Py-GC/MS system operated at 500 °C. A fixed catalyst-to-feed mass ratio of 1 was used in all experiments. In accordance with Nokkosmaki *et al.* [142], ZnO was found to be a mild catalyst showing a negligible activity. CaO significantly reduced the amounts of anhydrosugars, phenols, and acids. It also increased the formation of cyclopentanons, hydrocarbons and light products including acetaldehyde, 2-butanone, and methanol. Fe₂O₃ resulted in the formation of various hydrocarbons, mainly PAHs. In the same experimental system but with a different catalyst-to-feed ratio of 2, Lu *et al.* [145] (entry no.10 in Table A.2.6) conducted the catalytic upgrading of poplar wood-derived pyrolysis vapours using three commercially available TiO₂ (rutile), TiO₂ (anatase) and ZrO₂/TiO₂ (a mix. of 40 *wt.%* TiO₂ (anatase) and 60 *wt.%* ZrO₂), and their modified counterparts with the incorporation of Ce, Ru, or Pd. TiO₂ (rutile) and its Pd-containing counterpart (Pd- TiO₂) were found to be the most effective catalysts in converting lignin-derived oligomers to monomeric phenolic compounds due to enhanced cracking activity by the incorporation of Pd, with reduced amounts of aldehydes and sugars, increased amounts of ketones, acids, and cyclopentanons. The ZrO₂-TiO₂ catalysts remarkably reduced the phenol and acid yields with complete elimination of sugars, but increased the amounts of hydrocarbons, light linear ketones and cyclopentanons.

Torri *et al.* [110] (entry no.2 in Table A.2.6) used a novel Py-GC-MIP-AED system (pyrolysis-gas chromatography-microwave induced plasma-atomic emission detector) to evaluate and compare the performance of various metal oxides for catalytic pyrolysis of pine wood at 500 °C. CuO, ZnO, and mixed metal oxide catalysts significantly reduced the proportion of the heavy fraction in the bio-oil with minimum reduction in the bio-oil yield. CuO exhibited the highest yields in semi-volatile compounds.

Wang *et al.* [146] (entry no.1 in Table A.2.6) have performed *in situ* catalytic pyrolysis of pine wood, spruce wood (Alaskan) and lauan wood (tropical) in a bubbling fluidized bed reactor in the presence of alumina supported NiMo and CoMo catalysts. CoMo/Al₂O₃ (Criterion-534) is generally known to promote deoxygenation reactions when operating at high pressures in the presence of hydrogen. However, the effect of this catalyst during CFP of

biomass at atmospheric pressure without hydrogen is not well understood [44]. In this study, the CoMo/Al₂O₃ catalyst produced the highest yield of light aromatics whilst NiMo/Al₂O₃ produced the highest amount of methane. Maximum yield of BTXN (benzene, toluene, xylene, naphthalene) was achieved with CoMo-S/Al₂O₃ catalyst as 6.3 wt.% at 600 °C.

Due to their excellent resistance to coke formation and high acidity, metal-based catalysts can be promising alternatives for the production of upgraded bio-oil via CFP. Stefanidis *et al.* [147] (entry no.16 in Table A.2.4, entries no.13 and 23 in Table A.2.6) studied the ex situ upgrading of beech wood originated pyrolysis vapours in a bench scale packed-bed reactor at 500 °C. Among various catalysts, including commercial ZSM-5 formulations, metal oxides (*i.e.* MgO, NiO), and metal catalysts, *i.e.* alumina, tetragonal zirconia, titania, and Zr/Ti, the activity of catalysts based on aromatics selectivity was in the following order: alumina > Zr/Ti > ZSM-5. However, alumina and Zr/Ti were not found to be efficient catalysts since they resulted in too low yields of organic fraction (5.5 and 14 wt.%, respectively). But, they were shown to be promising catalysts for the removal of oxygen from bio-oil. ZSM-5 was the most suitable catalyst with a good selectivity toward aromatic compounds and acceptable yield of organic fraction (20.8 wt.%).

To date, microporous acidic zeolites and mesoporous materials have been extensively studied in the literature of CFP of lignocellulosic biomass. However, some drawbacks as the result of the utilization of these catalysts in CFP, such as the coke deposition and the formation of PAHs in case of microporous acidic zeolites, poor hydrothermal stabilities and high production costs related with the mesoporous materials have been observed. In order to alleviate these problems to some extent, several researchers have tested a variety of metal catalysts for CFP of woody biomass, as summarized in Table A.2.6 in the Supporting Information. It should be noticed here that the effects of alkali and alkaline earth metals (AAEMs) in the catalytic pyrolysis conditions are extensively detailed in Chapter 6 in this thesis; as the results of our own experiments.

2.4 Pilot-scale developments in CFP of biomass

Although laboratory studies regarding the catalytic fast pyrolysis of biomass have been carried out for more than two decades, the technology development is still in its infancy. The most serious commercial attempt up to date was KiOR Inc.'s. The company built the first commercial scale CFP facility in Columbus (Mississippi, USA), which started production in 2012. The selected process technology was based on existing Fluid Catalytic Cracking (FCC) technology, used for crude oil refining. The reactor was composed of a riser, a solid separator, and a catalyst regenerator, continuously operating in in situ mode (Fig. 2.6). The facility is designed as an initial scale commercial facility; processing 500 bone dry tons of woody biomass per day. It should produce over 13 million gallons of gasoline, diesel, and fuel oil blend-stocks annually, enough to fuel 25,000 cars. The company will next look to constructing its "flagship" facility in Natchez, Mississippi; it is designed to process approximately 1,500 bone dry tons of feedstock per day – three times the size of its Columbus facility – to take advantage of economies of scale [148]. On November 2014, KiOR Inc. filed for bankruptcy protection with a plan to sell its assets [149].

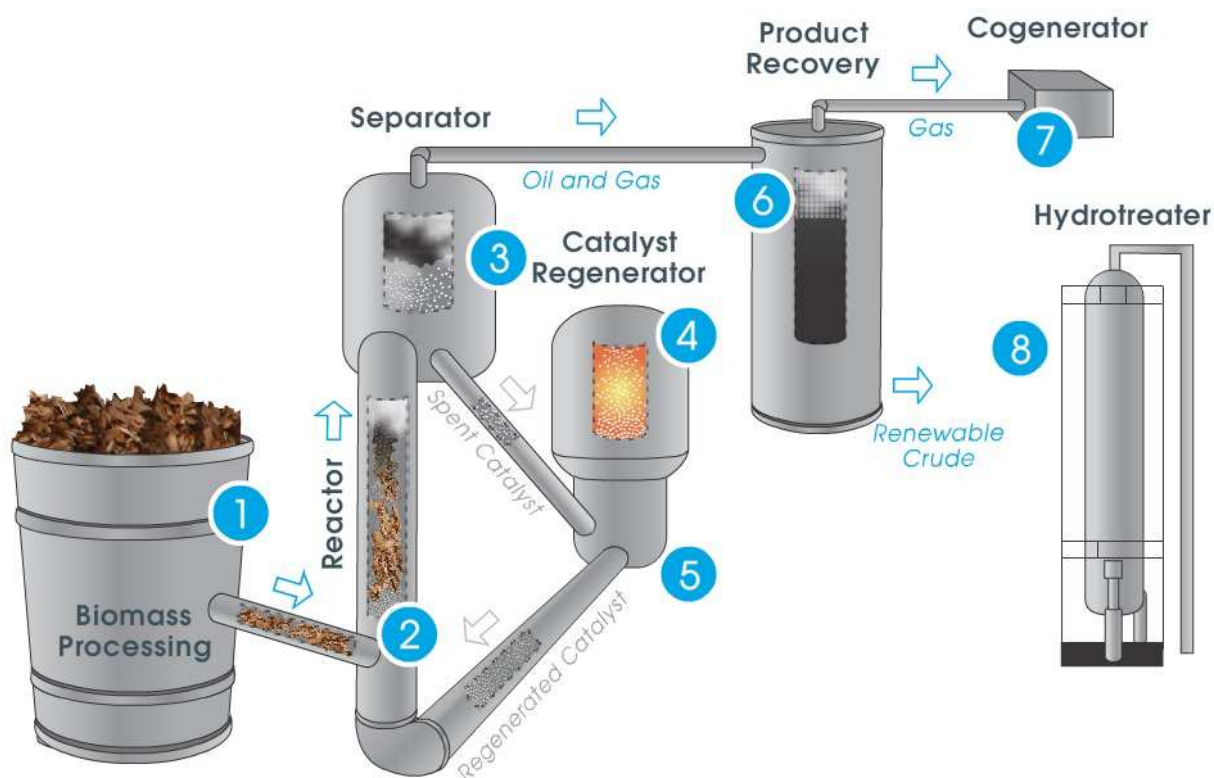


Fig. 2.6. The schematic of KiOR's process [150].

Anellotech is a spin-off company and was founded in 2008. The company has the exclusive license from the University of Massachusetts for the core Catalytic Fast Pyrolysis (CFP) process technology developed in the Huber lab. The first application of the technology, Biomass to AromaticsTM (BTA), is said to produce "green" benzene, toluene, and xylenes (BTX) in the future. The reactor technology is similar to that of KiOR's and composed of a fluidized bed reactor operating in combination with a catalyst separator and a catalyst regenerator [151]. Although is not mentioned anywhere, the process mode supposed to be in situ. With the successful start-up of its Pearl River pilot plant (erected in March 2013), Anellotech is now able to meet its commitment to provide BTX developmental quantities for evaluation by a number of strategic partners who invested in the development of the process. At this pilot plant, the company is currently producing kilogram-scale BTX directly from non-food biomass such as palm wastes, bagasse, corn stover, and even from wood feedstocks. If all goes according to schedule, Anellotech expects to start up its first commercial plant in 2019-2020.

Being a semi-commercial application of a catalytic hydropyrolysis process, the IH² technology is meant to provide a cost-effective route, ~\$2.00/gallon in 2012 dollars at 2000 mt dry feed/day scale, to produce fungible liquid hydrocarbon transportation fuels from renewable resources. This process was developed by the Gas Technology Institute (GTI) of Des Plaines, IL. GTI has licensed the IH² technology to CRI Catalyst Company (CRI) for exclusive worldwide deployment. The process involves the hydrodeoxygenation of the volatilized biomass to produce a raw hydrocarbon product over proprietary CRI catalysts in the presence of low-pressure hydrogen, followed by a fixed bed hydrotreater, which uses other proprietary CRI catalysts to polish the first-stage product and transform it into a finished

hydrocarbon fuel or blend stock. As a step in the commercialization process, GTI commissioned a new 50 kg/day Pilot-Scale IH² Plant in the first quarter of 2012. The goal of the pilot plant studies is to provide validation of the operational and performance factors that are key to achieving commercial deployment in 2014 [152–155].

Unfortunately the precise performance of the larger plants in terms of product yields, the information regarding the product quality (*e.g.* acidity, viscosity, chemical composition), and total operation time remains obscure. Websites of private enterprises do not mention such data although it appears that the companies are sending out larger samples for closer inspection by future clients.

Chapter 3

Validation of a new set-up for continuous catalytic fast pyrolysis of biomass coupled with vapour phase upgrading

Abstract

A fully controlled, continuously operated mini-plant has been designed and constructed based on auger reactor technology. Three types of biomass fast pyrolysis experiments were performed in this set-up, viz. non-catalytic, in situ catalytic fast pyrolysis and ex situ upgrading of non-catalytic fast pyrolysis vapours by means of a downstream, moving-bed catalytic reactor. Pine wood was selected as the reference biomass feedstock. The mini-plant enables variation of the catalyst loading and contact times while producing larger samples suitable for full characterization in continuous operation. Due to short catalyst residence times and the fact that the biomass fed to the reactor is always brought into contact with fresh catalyst (in case of in situ catalysis) or the pyrolysis vapours always contact with fresh catalyst in the moving bed catalytic reactor (in case of ex situ catalysis), catalyst deactivation and coking are prevented ensuring improved experimental repeatability in catalytic pyrolysis experiments. The performance of the system was verified by in and ex situ application of a single type of heterogeneous ZSM-5 based acidic catalyst while the non-catalytic results were taken as reference. Catalytic fast pyrolysis results in more effective oxygen removal from the bio-oil in the form of water, and resulting in lower yields of the organic fraction. Moreover catalytic decarbonylation reactions gave rise to increased gas yields. With in and ex situ catalysis, increases in the char yields were observed as well as coke deposition on the catalyst surface. GC×GC–FID and GC×GC–TOF–MS analysis of the produced bio-oils showed that the use of in and ex situ catalysis causes conversion of high molecular weight compounds to lower ones. Disappearance of detectable sugars and aldehydes, a decrease of the yield of acids, formation of phenols, and favoured aromatics production were the other catalytic effects observed.

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3.1 Introduction

Fast pyrolysis intends to convert biomass into a maximum quantity of transportable liquids that can be used for the production of energy (*i.e.* heat, power), chemicals, and/or biofuels [29,178]. The process is characterized by the rapid heating of biomass particles to a moderate temperature of approximately 500 °C, followed by the instant condensation of the produced vapours. The latter results in a maximum quantity of dark-brown liquid (the so-called bio-oil or pyrolysis oil) with a heating value roughly equal to that of the dry biomass (18–21 MJ/kg), which is almost half the heating value of petroleum [30]. A critical review regarding the production and properties of bio-oil is documented elsewhere [29].

Crude bio-oil is a mixture of hundreds of different, oxygen containing organic compounds. It is unsuitable for direct application as a transportation fuel due to its adverse properties (*e.g.* instability, acidity, and corrosiveness) caused by the various undesired oxygen functionalities in virgin bio-oil. The amount of oxygen present in bio-oil is important, but also the way in which oxygen is bound in the bio-oil compounds (acids, ketones, aldehydes, furans, sugars, phenols, *etc.*). To improve the quality of crude bio-oil for biofuel applications and to reduce the upgrading costs, fast pyrolysis of biomass can be carried out in the presence of suitable catalysts (*i.e.* catalytic fast pyrolysis; CFP) [74].

In CFP of biomass, the catalytic treatment can either be *in situ*, *i.e.* adding catalyst particles to the reactor, or *ex situ*, *i.e.* secondary conversion of the produced vapours of fast pyrolysis. The desired function of the catalyst, in both cases, is the catalytic cracking of high molecular weight vapour phase compounds into smaller ones (anhydrosugars to furans, furans to olefins, *etc.*). The ultimate goal of the CFP is the removal of oxygen in the form of CO, CO₂, and H₂O by steering the oxygen containing chemical functionalities in pyrolysis vapours (see Chapter 2 in this thesis). Reports from NREL show that crude bio-oil upgraded by hydro-deoxygenation (HDO) process can be produced at a very competitive price compared to other biomass conversion technologies [179]. Eventually, the product oil fraction produced by catalytic fast pyrolysis (*i.e.* CFP-oil) will contain less oxygen and requires, if at all, a far milder HDO treatment with less hydrogen consumption and thus, a cheaper HDO process can be achieved.

In the present article, the focus is on the comparison of the properties and composition of CFP-oils produced with *in situ* and *ex situ* CFP of biomass with a single type of catalyst. The CFP experiments were performed in a dedicated mini-plant that allows variation of the catalyst loading and contact times while producing larger bio-oil samples in continuous operation. Particular attention is paid to the catalyst capabilities to suppress coke and gas formation, to reduce oxygen and modify its functionalities in the bio-oil and to increase the yield of the hydrocarbon fraction. The latter could be used for co-feeding petroleum refinery units in the production of transportation fuels [85].

3.2 Materials and methods

3.2.1 Materials

Pine wood was obtained from Bemap Houtmeel B.V. (Bemmel, Netherlands) and selected as reference biomass feedstock. The moisture content was 8.45 wt.% (as-received basis, a.r.) and the number-average particle size was 1 mm (maximum size = 2 mm). The elemental composition of the pine wood together with the proximate analysis data are listed in Table 3.1.

Silica sand with a mean diameter of 250 μm and a particle density of 2650 kg/m^3 (compacted bulk density = 1660 kg/m^3) was obtained from PTB-Compaktuna (Gent, Belgium).

A heterogeneous ZSM-5 based acidic catalyst, indicated as ‘Type A’ was prepared and supplied by Albemarle Catalyst Company B.V. (Amsterdam, The Netherlands) for the in situ and ex situ pyrolysis experiments. Physical and chemical properties of this catalyst can be found in Appendix A (this appendix is confidential and can only be accessed by signing a confidentiality agreement). To minimize the water accumulation in the final liquid product, this catalyst was calcined in air at 500 °C for 1 h to decrease the catalyst bound/absorbed moisture content to below 1 wt.%.

Table 3.1. Properties of biomass used.

Proximate analysis (wt.%)	
Fixed carbon (d.b.)	14.96
Volatiles (d.b.) [ASTM E872-82]	84.76
Moisture (a.r.) [ASTM E871-82]	8.45
Ash (d.b.) [ASTM E1755-01]	0.1
Ultimate analysis (d.b.) [wt.%]	
C	47.1
H	5.9
O	39.7
N	0.04
S	0.06
Alkali metals (d.b.) [mg/kg]	
K	346.2
Na	10.1
Mg	112.8
Ca	767.0
HHV (d.b) [MJ/kg]	19.1

3.2.2 Fast pyrolysis mini-plant

Fast pyrolysis experiments were carried out in a fully controlled, continuously operated mini-plant designed and constructed by Biomass Technology Group B.V., BTG (Enschede, The Netherlands) based on the auger reactor technology. The mini-plant enables the production of larger bio-oil samples (typically 0.3 kg/h) suitable for a full characterization, even in the case of phase-separated bio-oil. Table 3.2 shows the design specifications of the mini-plant. Three types of biomass fast pyrolysis experiments can be performed in this system, *viz.* non-catalytic (using hot sand as the heat carrier), in situ catalytic (using mixtures of sand and catalyst as heat carrier) and ex situ catalytic (vapour phase upgrading) fast pyrolysis experiments. This mini-plant is schematically shown in Fig. 3.1.

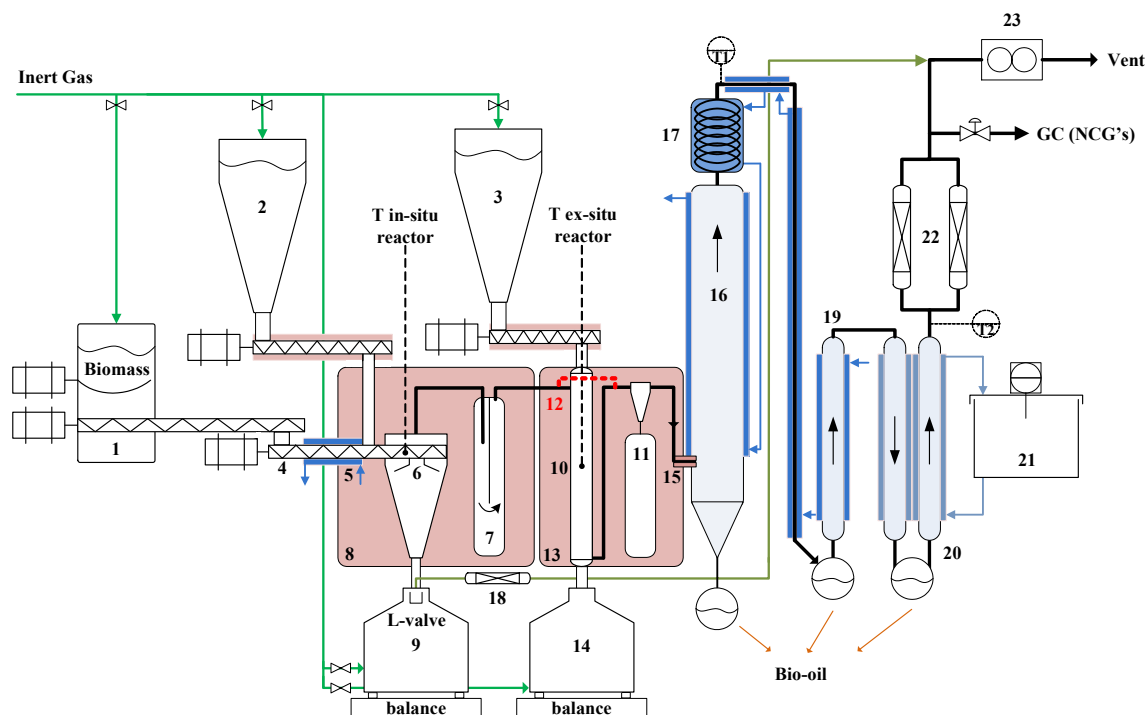


Fig. 3.1. Schematic drawing of the mini-plant: (1) biomass storage hopper; (2) heat carrier storage hopper; (3) catalyst–sand mixture (for ex situ runs) storage hopper; (4) auger screw; (5) cooling jacket; (6) in situ reactor; (7) knock-out vessel; (8) in situ reactor oven; (9) solids collection vessel; (10) ex situ reactor; (11) ex situ cyclone; (12) by-pass line; (13) ex situ reactor oven; (14) spent catalyst collection vessel; (15) condenser inlet heater; (16) cold trap condenser tower; (17) stainless steel spiral condenser; (18) gas filter; (19) tap water cooled spiral glass condensers; (20) ethylene glycol cooled spiral glass condensers; (21) refrigerated cooler; (22) cotton filters; and (23) gas flow indicator. Green: N₂ lines; pink: heated zones; blue: cooled zones.

Table 3.2. Design specifications of the mini-plant.

Technology	Catalytic fast pyrolysis
Experimental modes	Non-catalytic, in situ, ex situ
Max. temperature [°C]	600
Max. biomass feed flow rate [g/h]	500
Max. heat carrier flow rate (in situ) [kg/h]	10
Max. catalyst (blend) flow rate (ex situ) [kg/h]	3
Max. inert gas flow rate [L/h]	150
System pressure	Atmospheric
Biomass residence time (with the heat carrier) [s]	<i>ca.</i> 1
Hot vapour residence time [s]	<i>ca.</i> 5

The biomass (a.r.) is stored in a storage hopper with a capacity of 4 kg (*no.* 1). To prevent biomass particles from aggregating and forming bridges, a stirrer inside the hopper rotates during the run. The biomass feeding screw, connected to the biomass hopper, is used to transport biomass to the auger reactor. A hopper with a capacity of 25 kg in combination with a 110 cm long heated screw (*no.* 2) is used for the transport of the heat carrier to the auger reactor. Sand is used for the non-catalytic and ex situ catalytic experiments, while catalyst–sand mixtures are used for the in situ catalytic experiments. The auger reactor is operated as the main unit for the biomass fast pyrolysis. The last section of this screw where the biomass and heat carrier are intensively mixed with a residence time of *ca.* 1 s is called the “pyrolysis reactor” or “in situ reactor” (*no.* 6). A water-cooled stainless steel jacket (*no.* 5) was placed to the fore section of the auger to prevent biomass decomposition before contact with the heat carrier. During the run, produced vapours are entrained to the knock-out vessel (*no.* 7) by the continuous inert gas flow (N₂) and the heat carrier and char particles fall down to the solids collection vessel (*no.* 9). In the solids entrance of the vessel a special type of valve (L-valve) is placed. This valve is a bent pipeline that slows down the solids flow and allows an additional solid hold-up to increase the contact time of charred biomass with the hot heat carrier. This allows maximizing the devolatilization of the biomass particles.

For ex situ catalytic experiments, the non-catalytic fast pyrolysis vapours produced in the pyrolysis reactor are carried to the vapour phase upgrading reactor (ex situ reactor) (*no.* 10) after passing the knock-out vessel. The catalyst–sand mixture flows from the storage hopper through a 60 cm long heated screw (*no.* 3) to the ex situ reactor (moving bed reactor) where the vapours are co-currently contacted with this preheated catalyst–sand mixture with a residence time of *ca.* 3 s. A collection vessel (*no.* 14) is put underneath the ex situ reactor oven. To prevent the escape of the vapours to the collection vessels, these are purged with inert gas (N₂) during the run. Analytical balances (Sartorius, Combics CW1P1, accuracy ±2 g) measure the weight increase of both collection vessels.

The inlet line to the condenser is heated to prevent local tar accumulation (*no.* 15). In the present study a cold-trap condenser system was used to condense the pyrolysis vapours into bio-oils. This system consists of a condenser tower (*no.* 16), a stainless steel spiral condenser (*no.* 17), vapour transfer pipelines, and a spiral glass condenser (*no.* 19). All these combined parts are tap water cooled and jacketed. The outgoing stream passes through two ethylene glycol cooled spiral glass condensers (*no.* 20). An ethylene glycol refrigeration unit (*no.* 21) was used to keep the temperature of these two spiral glass condensers constant at -25°C . The remaining vapours and gases pass through the cotton filters (*no.* 22). These are installed to maximize liquid collection. The volumetric flow rate of the non-condensable gas leaving the cotton filters is measured with a dry gas flow indicator (Itron, Gallus 2000 G1.6, accuracy is 10^{-4} Nm^3) (*no.* 23).

In the mini-plant, several thermocouples and pressure sensors are installed to continuously monitor the temperature and pressure at various points. In order to increase the accuracy of the measurements and minimize the errors the changes in temperatures, pressures and flow rates are observed and controlled online via the Advantech ADAMView system software. The temperature in the last section of the auger reactor where the pyrolysis reactions take place is defined as the in situ reactor temperature, $T_{\text{in situ reactor}}$. In the secondary reactor, meant for ex situ vapour upgrading, three thermocouples are installed at different heights and the average value is taken as the ex situ reactor temperature, $T_{\text{ex situ reactor}}$. These two temperatures are used as the set points for the ovens' (nos. 8 and *no.* 13) (Westeneng Ovenbouw B.V.) control loop.

3.2.3 Experimental procedure

Prior to each experimental run, the fresh biomass sample (a.r.) was weighed on an analytical balance (Kern, FCB 3K, accuracy $\pm 0.1 \text{ g}$) and loaded into the biomass hopper. For non-catalytic experiments, a known amount of sand of *ca.* 20 kg, for in situ catalytic experiments a known amount of catalyst-sand mixture of *ca.* 20 kg (catalyst-to-sand ratio 1:4/w:w) and for the ex situ catalytic experiments a known amount of mixture of *ca.* 3 kg (catalyst-to-sand ratio was 3:1/w:w) were weighed (Sartorius, Combics CW1P1, accuracy $\pm 2 \text{ g}$), and loaded to the hoppers. In order to get fixed and repeatable catalyst-to-biomass ratios, the biomass flow rate and the catalyst-to-sand ratios were optimized by performing several blank experiments. The total quantity of materials fed during a run was determined by measuring the mass difference of these materials in the hoppers and in the feeding screws before and after an experiment. A controlled flow of inert gas (N_2 , Air Liquide, purity $\geq 99.9\%$) was fed to all hoppers to ensure an inert atmosphere inside the system and transfer the produced vapours through the system. To minimize secondary reactions it is important to have vapour residence times of typically less than 2 s [29]. Hence, during non-catalytic and in situ catalytic experiments the ex situ reactor and the ex situ cyclone were by-passed to shorten vapour residence times.

After making all connections within the system a pressure test was carried to verify the absence of possible leaks. Next, the heating was started under an inert atmosphere. The inert gas flow rate was measured by reading the gas flow indicator output which is located just before the vent.

Once the system reached the desired temperature, the auger reactor, and the heat carrier conveyors were switched on and the heat carrier (and the catalyst–sand blend for ex situ experiments) inside the separate hoppers were conveyed through the reactors. The experiments were started by turning on the biomass feeding screw when the system reached its steady state after approximately 30 min.

3.2.4 Pyrolysis products analysis

3.2.4.1 Non-condensable gases

The inert gas flow supply is set by 5 separate mass flow controllers (Kobold, type KDG) that control the flow through the hoppers and vessels. The total volume of outlet gas is measured every five minutes using a gas flow indicator (in Nm³, precision is 10^{−4} Nm³). The average non-condensable gas flow rate ($\Phi_{g,avg}$; L/h) is the difference between the total average gas flow rate during the run, measured at the mini-plant's gas outlet and the average inert gas flow rate before feeding biomass (Eq. 3.1):

$$\Phi_{g,avg} = \frac{\left. \frac{readout_{final} - readout_{initial}}{(t_{final} - t_{initial})} \right|_{total\ gas}}{\left. \frac{readout_{final} - readout_{initial}}{(t_{final} - t_{initial})} \right|_{inert\ gas}} \quad (Eq. 3.1)$$

During the run, specified as t_{run} (min), eight gas samples were taken at intervals of 10 min by using a gas-tight syringe. These were analysed off-line using a Varian Micro-GC 490-GC with two analytical columns; 10 m Molesieve 5A (with backflush) and 10 m PPQ with TCD detectors, using Helium and Argon (Alphagaz) as carrier gases. In order to minimize the errors on measurements, this device was calibrated prior to each experiment by using two different gas mixtures with known component quantities. The following compounds were measured by the micro-GC: H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈. The sum of C₂H₄, C₂H₆, C₃H₆ and C₃H₈ will be further referred to as C₂₊.

The total non-condensable gas yield is calculated by summation over the yields of the individual gas compounds and dividing this value by the amount of biomass (a.r.) fed during the run (Eq. 3.2).

$$Y_{gas} = \left[\sum_i \frac{MW_i \cdot (vol\%_i / vol\%_{total}) \cdot t_{run} \cdot \Phi_{g,avg}}{(R \cdot T_g \cdot 60 / P \cdot 100)} \right] \cdot \frac{100\%}{M_{feed}} \quad (Eq. 3.2)$$

3.2.4.2 Char

To determine the produced amount of char, the char/heat carrier mixture collected in the solids collection vessel needs to be sieved. The first step is sieving by hand followed by a subsequent mechanical sieving in a shaker (Retsch AS 200; Edelstahl test sieve with 0.25 mm aperture). The separated char still contains a significant portion of sand and/or catalyst particles that adhere to the char's surface. Thus the char and heat carrier mixture were subjected to loss on ignition analysis (burning under air atmosphere in a Carbolite muffle oven AAF 1100, at 600 °C, 6 h) and the masses of char and sand in this mixture were

determined. Before the loss on ignition analysis, small amounts of char were taken and the elemental analysis was carried out with a Thermo Scientific Flash 2000 Organic Elemental Analyser.

The char yield (a.r.) was calculated by dividing the mass of char that was lost during the loss on ignition analysis by the amount of biomass fed during the run (Eq. 3.3). Hence, all non-volatile ash compounds are expected to be either on the catalyst or sand.

$$Y_{char} = [(M_{solid\ mix} \cdot wt\%_{char\ in\ mix})] \cdot \frac{100\%}{M_{feed}} \quad (Eq. 3.3)$$

3.2.4.3 System carbon

System carbon consists of the coke on the non-catalytic/in situ heat carrier and ex situ spent catalyst, knock-out vessel/cyclone solids and the filtrated solids from bio-oil. These solid fractions were separately collected, weighed and analysed in terms of their carbon content (assuming that coke is mainly composed out of carbon) by means of loss on ignition analysis. The system carbon yields were calculated using the formulae below:

For the non-catalytic and in situ catalytic experiments (Eq. 3.4):

$$Y_{system\ carbon} = \{[(M_{hc,i} - M_{hc,f}) \cdot (wt\%_{hc,coke})] + [M_{kvs} \cdot (wt\%_{kvs,coke})] + [M_{filtrate} \cdot (wt\%_{filtrate,coke})]\} \cdot \frac{100\%}{M_{feed}} \quad (Eq. 3.4)$$

for the ex situ experiments (Eq. 3.5):

$$Y_{system\ carbon} = \{[(M_{hc,i} - M_{hc,f}) \cdot (wt\%_{hc,coke})] + [M_{kvs} \cdot (wt\%_{kvs,coke})] + [(M_{ex\ situ\ cb,i} - M_{ex\ situ\ cb,f}) \cdot (wt\%_{sc,coke})] + [M_{cs} \cdot (wt\%_{cs,coke})] + [M_{filtrate} \cdot (wt\%_{filtrate,coke})]\} \cdot \frac{100\%}{M_{feed}} \quad (Eq. 3.5)$$

3.2.4.4 Bio-oil

Subsequent to each experiment, the bio-oils collected in the cold-trap condenser parts (including the cotton filters) were removed by flushing with tetrahydrofuran (THF). The use of this solvent allowed the complete collection of the bio-oil heavy fractions that are stuck on the condenser walls and in the vapour pipelines. Collecting all the produced liquids (heavy and aqueous phases) in a homogeneous single phase helped to determine the liquid yield more precisely and also increased the stabilization of bio-oil. The collected bio-oil/THF mixture was later analysed via a GC×GC–FID in terms of its THF content which was used to determine the total liquid yield (Eq. 3.6). Also, the moisture content of the catalyst was determined via the moisture analysis and the excess amount of water that ends up in the condensed liquids was excluded from the total amount.

$$Y_{liquid} = \left\{ \left[M_{liq.mix} \cdot \left(1 - \frac{wt\%_{THF \text{ in } liq.mix}}{100} \right) \right] - \left[(M_{hc,i} - M_{hc,f}) \cdot \left(\frac{wt\%_{moisture,hc}}{100} \right) \right] \right\} \cdot \frac{100\%}{M_{feed}} \quad (Eq. 3.6)$$

For the detailed characterization of bio-oils, a combination of GC×GC–FID and GC×GC–TOF–MS was used to get a high chromatographic resolution and on the other hand maximal agreement between both chromatograms [180]. The GC×GC setup was consisted of a Thermo Scientific TRACE GC×GC, obtained from Interscience Belgium and has been discussed previously [181,182]. The setup is equipped with both an FID and a TEMPUS TOF–MS (Thermo Scientific, Interscience Belgium) detectors. Injection volume was 0.2 µl, with a split flow of 150 ml/min, and an injector temperature of 280 °C. The first column was a Rtx-1 PONA (50 m L × 0.25 mm I.D. × 0.5 µm df) and the second column was a BPX-50 (2 m L × 0.15 mm I.D. × 0.15 µm df). Oven temperature programme started at –40 °C and was ramped up to 300 °C at a heating rate of 3 °C/min. For GC×GC, the modulation period was 7 s. A built-in switching system, *i.e.* a 4 port 2 way valve (VICI AG International, Switzerland) allowed to switch between the FID and MS detectors without the need to cool down and vent the TOF–MS [181,182].

For the elemental analyses an elemental analyser (Thermo Scientific Flash 2000 equipped with an AS3000 liquid auto sampler) was used.

The collected oils were analysed in terms of their water content by Karl Fischer Titration (Mettler Toledo V20 with 5 ml burette; electrode: DM 143-SC; reagent: Merck Combi Titrant 5 Keto; solvent: Merck Combi Solvent 5 Keto). The water yield was calculated using the formula (Eq. 3.7):

$$Y_{water} = (w_{liq.mix} \cdot df) \cdot \frac{M_{liquid}}{M_{feed}} \quad (Eq. 3.7)$$

where

$$df = \frac{1}{1 - (wt\%_{THF \text{ in } liq.mix.}/100)} \quad (Eq. 3.8)$$

The organic liquid yield was simply calculated as (Eq. 3.9):

$$Y_{organic \ liquid} = Y_{liquid} - Y_{water} \quad (Eq. 3.9)$$

The acidity of the oil samples was analysed in terms of TAN (total acid number, in mg KOH/g liquid) (Metrohm 848 Titrino-Plus; titrant: KOH, 0.1N; solvent: propan-2-ol and toluene, combined glass (pH) electrode, incorporated reference system LiCl saturated in ethanol). The total acid number of the liquid product was calculated using the formula (Eq. 3.10):

$$TAN = (a_{liq.mix} \cdot df) \quad (Eq. 3.10)$$

3.2.4.5 Mass balance

The mass balance within the system was calculated by using the equation below:

$$Y_{total} = Y_{organic\ liquid} + Y_{water} + Y_{gas} + Y_{char} + Y_{system\ carbon}$$

that is equal to (Eq. 3.11):

$$Y_{total} = (M_{organic\ liquid} + M_{water} + M_{gas} + M_{char} + M_{system\ carbon}) \cdot \frac{100\%}{M_{feed}} \quad (Eq. 3.11)$$

3.3 Results and discussions

3.3.1 Mass balance closure and reproducibility

The reproducibility of the mini-plant was verified by carrying out 8 non-catalytic experiments. During these experiments at a constant temperature of 500 °C, no operational problems were encountered. Operating conditions for non-catalytic experiments are reported in Table 3.3.

Table 3.3. Operating conditions non-catalytic experiments.

	<i>Range</i>	<i>Average</i>
Fast pyrolysis temperature [°C]	500	500
Experimental run time [min]	110 – 210	170
Biomass feed rate [g/h]	180 – 248	200
Inert gas flow rate [L/h]	-	120
Heat carrier flow rate [kg/h]	5.3 – 6.6	5.9
Heat carrier/biomass ratio [wt./wt.]	22.5 – 30.7	26.8

The mass balance closure of the non-catalytic tests varied between 96.5 wt.% and 102.1 wt.%. The average yields on as received basis are reported in Fig. 3.2. Of these tests the average yields are 58.9 wt.% for pyrolysis oil (organics + produced water), 22.2 wt.% for non-condensable gases, 15.9 wt.% for char, and 2.6 wt.% for system carbon, respectively. These yields are within the range of fast pyrolysis of wood reported in the literature [29] and proof that the setup is truly a fast pyrolysis setup.

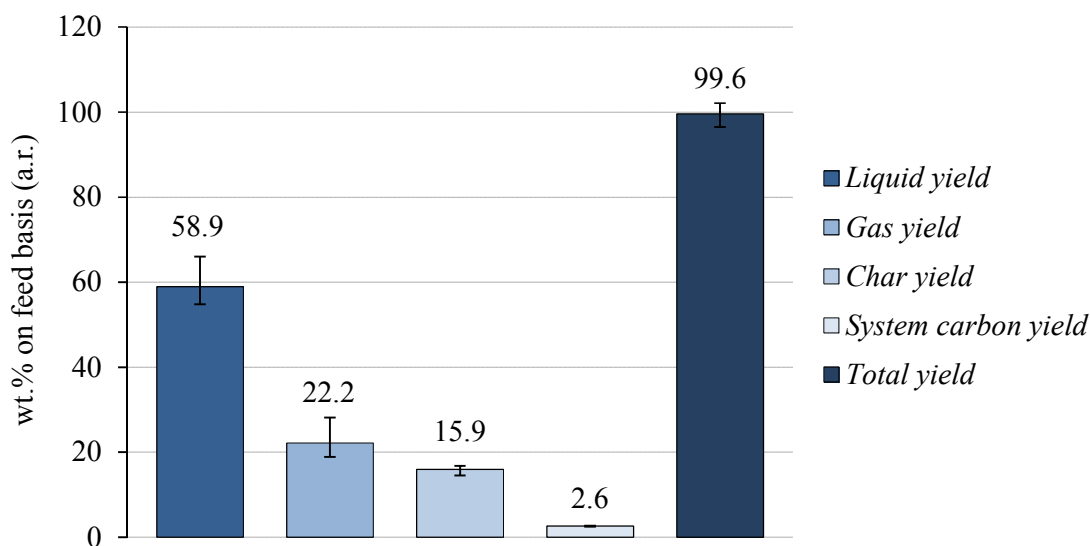


Fig. 3.2. Average yields of liquid, non-condensable gas, char and system carbon obtained from 8 non-catalytic fast pyrolysis experiments of pine wood at 500 °C.

The error bars shown in the graphs represent the minimum and maximum values over all experiments. The scatter on the liquid, char, and gas yield is less than 7 %, denoting that the reproducibility of the experiments is acceptable and low enough for trend detection.

3.3.2 In situ/ex situ catalytic pyrolysis versus non-catalytic pyrolysis

In total, 5 in situ and 5 ex situ experiments were carried out using the same type of catalyst. Operating conditions of the catalytic experiments are given in Table 3.4. Experimental run time was kept at a minimum of 90 min in order to produce sufficient bio-oil for the different types of analyses as well as to reach a sufficiently high accuracy on the mass balance determination.

Table 3.4. Operating conditions catalytic experiments.

	<i>In situ</i>	<i>Ex situ</i>
Fast pyrolysis temperature [°C]	500	500
Catalytic reactor temperature [°C]	-	500
Experimental run time [min]	100	90
Biomass feed rate [g/h]	200	200
Inert gas flow rate [L/h]	120	120
Ratio of sand/catalyst in mixture [wt./wt.]	4:1	1:3
Heat carrier/biomass ratio [wt./wt.]	53.8	32.3
Residence time of vapours with catalyst [s]	<i>ca.</i> 1	<i>ca.</i> 3
Catalyst/biomass ratio [wt./wt.]	5	5

The liquid, char and solid product yields (wt.% based on biomass feed) obtained by the in situ and ex situ catalytic upgrading of lignocellulosic biomass pyrolysis products are visualized in Fig. 3.3. These values are compared to the yields obtained for the non-catalytic silica sand experiments. Apparently each catalytic material affects the product yields in its own way. The reason for the deviations was probably due to variations in heat carrier flow rate (Tables 3.3 and 3.4); however, the average yield values are comparable. Table 3.5 lists the average yields, standard deviations, and the relative spread ($\sigma_Y/Y \times 100\%$) of 8 non-catalytic, 5 in situ catalytic and 5 ex situ catalytic experiments. The relative scatter on the liquid, non-condensable gas, char, and system carbon yield is less than 10 %, showing that the reproducibility of the experiments is good. The relative spread on the yield of produced gas is somewhat larger for the non-catalytic and ex situ runs (11.5 % and 10.2 %, respectively), but is still low enough for trend detection. Higher standard deviations in system carbon yields of in- and ex situ catalytic experiments may be related to the collection and weighing errors of solid samples. Furthermore, a noticeable lower standard deviation of the ex situ liquid yield in comparison with the liquid yield of in situ and non-catalytic experiments was observed; this may be due to the lower tar formation in the condenser system which facilitates collection of the liquid product.

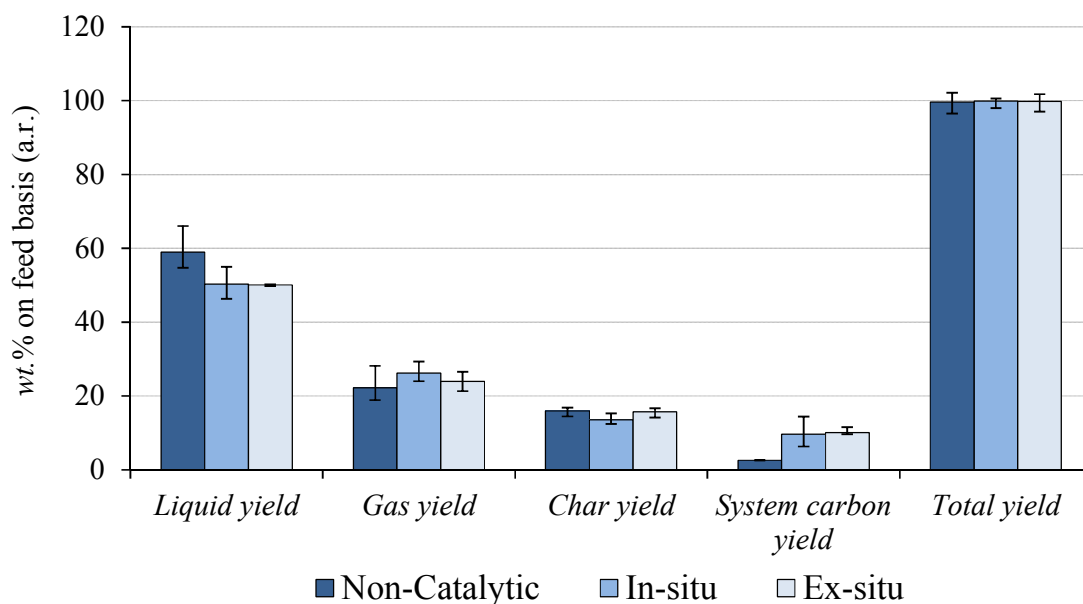


Fig. 3.3. Average yields of liquid, non-condensable gas, char and system carbon obtained from in situ and ex situ catalytic fast pyrolysis experiments, compared to the reference, non-catalytic experiments of pine wood at 500 °C.

Table 3.5. Reproducibility of eight identical non-catalytic, five identical in situ catalytic, and five identical ex situ experiments.

<i>Experiment mode</i>	<i>Product</i>	<i>Average yield, Y [wt.%]</i>	<i>Std. dev., σ_Y [wt.%]</i>	<i>Relative spread, $\sigma_Y/Y \times 100\%$ [%]</i>
Non-catalytic	Liquid	58.9	4.5	7.7
	Gas	22.2	2.6	11.5
	Char	15.9	1.1	7.0
	System carbon	2.6	0.1	5.5
In situ	Liquid	50.3	4.4	8.7
	Gas	26.2	2.4	9.0
	Char	13.6	1.2	9.1
	System carbon	9.7	0.9	8.9
Ex situ	Liquid	50.1	1.2	2.5
	Gas	23.9	2.4	10.2
	Char	15.7	1.0	6.2
	System carbon	10.1	0.8	8.0

With the catalyst application, a decrease of 8.6 wt.% for the in situ, and a decrease of 8.8 wt.% for ex situ modes were observed in terms of liquid yields. On the other hand, gas and system carbon yields increased with the catalyst addition and are significantly different enough to draw conclusions. For the in situ mode, a decrease of 2.3 wt.% in char yield was seen. This decrease in char yield in in situ mode was related to the higher heat carrier/biomass ratio that results in a higher conversion rate of biomass particles into vapours. In ex situ mode, a very slight decrease in char yield was observed with 0.2 wt.% compared to the non-catalytic mode. The reason for this very similar char yield in ex situ mode is due to the presence of the same fast pyrolysis conditions in the pyrolysis reactor. Gas yield increases of 4 wt.% and 1.7 wt.%, respectively for in situ and ex situ modes were observed. These changes in the product yields agree with literature [102,104]. Coke deposition on the heat carrier (sand and catalyst mixture) surface was observed by the change in colour from yellow to grey. It increased to 9.7 wt.% on feed basis for the in situ and to 10.1 wt.% on feed basis for the ex situ mode, taking the average coke deposition on the spent sand of the non-catalytic experiments as the reference case which was 2.6 wt.% on feed basis.

The use of catalyst led to a decrease in the liquid and organic product yields with a simultaneous increase in water yield. The organic yield decreased by 20.6 wt.% and 20.2 wt.%, while water yield increased by 13.5 wt.% and 13.7 wt.% for in situ and ex situ modes, respectively (Fig. 3.4). The catalysts increase dehydration reaction of the oxygenated species in the product and product vapours, thus the water yield in bio-oil is increased at the expense of organic liquid yield. Also, the formation of coke on the catalyst is responsible for large losses in biomass carbon and thus the reduction in the organic liquid yield.

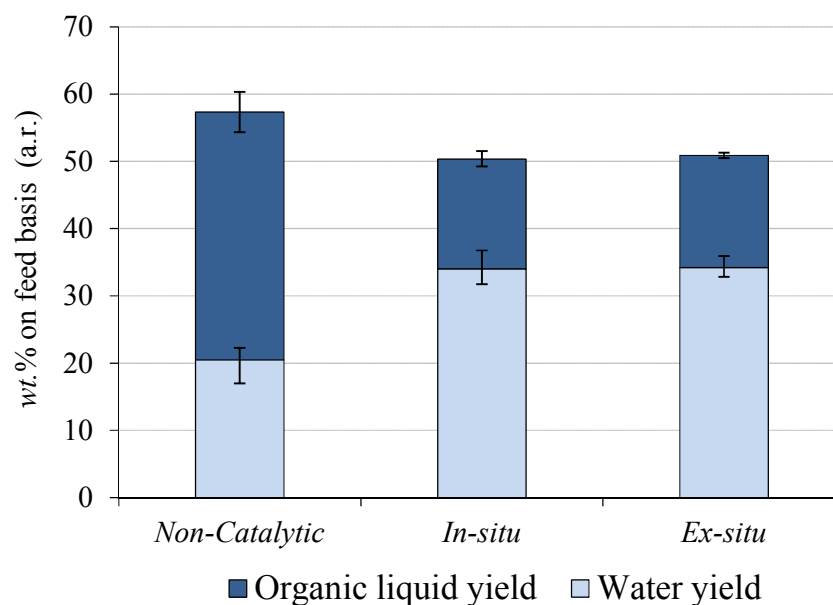


Fig. 3.4. Average organic liquid and water yields of liquid obtained from in situ and ex situ catalytic fast pyrolysis experiments, compared to the reference, non-catalytic experiments of pine wood at 500 °C.

Compared to non-catalytic runs, gas production increased in the presence of catalyst as CO₂ and CO were the main gaseous products. Other detectable compounds were H₂, CH₄ and C₂₊'s in comparatively smaller quantities. Fig. 3.5 shows the changes in composition of the non-condensable gas compounds for the different experimental modes. The higher yields in CO indicate that decarbonylation reactions were clearly favoured, as well as an increase in C₂₊ compounds were observed in the presence of catalyst. CO₂ yields were almost the same that shows the in- and ex situ application of this catalyst do not favour decarboxylation reactions. Also, slight decreases were observed in the CH₄ yields.

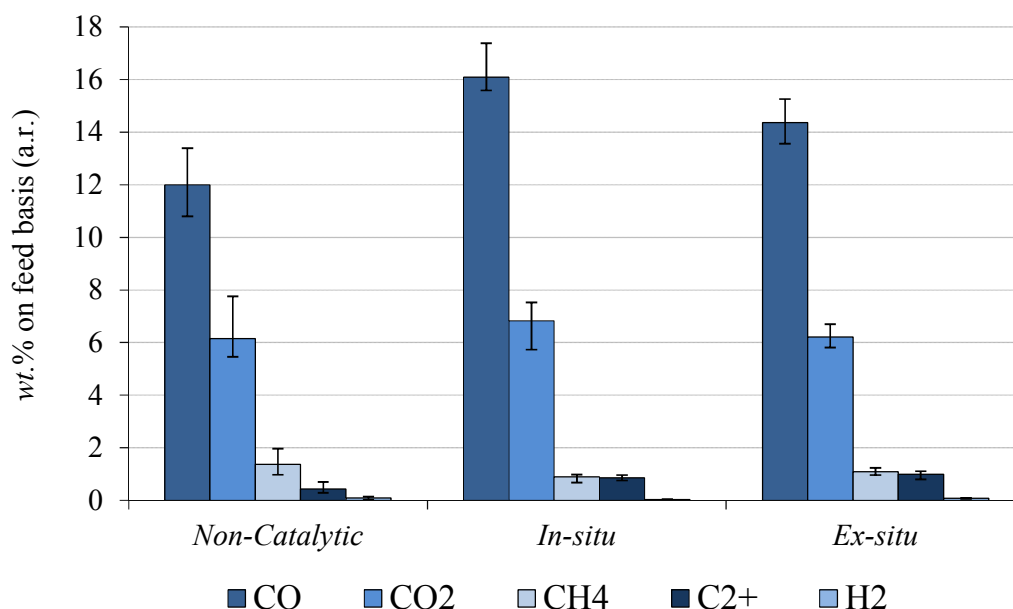


Fig. 3.5. Average composition of the non-condensable gas obtained from in situ and ex situ catalytic fast pyrolysis experiments, compared to the reference, non-catalytic experiments of pine wood at 500 °C.

Before pyrolysis oils are compatible with existing fuel infrastructure, they require catalytic upgrading to remove oxygen functional groups [70]. Oxygen is removed from the pyrolysis vapours in the form of CO, CO₂, and H₂O. In the case of CO formation, a single carbon atom is consumed to remove each oxygen atom, whereas the removal of oxygen in the form of CO₂ is the most preferable route because to remove two oxygen atoms only one carbon atom is consumed. Oxygen removal by the formation of H₂O is in turn less desirable than CO₂ or CO formation in order to preserve the highly energetic carbon–hydrogen bonds in the bio-oil constituents and also to preserve hydrogen for the catalyzed hydrocarbon forming reactions [147,183]. In combination with Figs. 4 and 5, it can be concluded that the prevalent mechanism for oxygen removal was dehydration for the catalytic modes. Decarbonylation mechanism contributed to oxygen removal in both in- and ex situ modes while in situ performance was better. The performance for decarboxylation mechanism of in situ mode was slightly better than that of ex situ which was similar to the non-catalytic case.

3.3.3 Chemical composition of the bio-oil

Fig. 3.6 shows the GC–MS based group type analysis of bio-oil by sorting the components into 8 chemical groups. High molecular weight compounds and the compounds whose group name is not available in the MS library were classified as ‘others’. Table 3.6 shows the changes of the most abundant compounds in the organic phase for the different experimental modes.

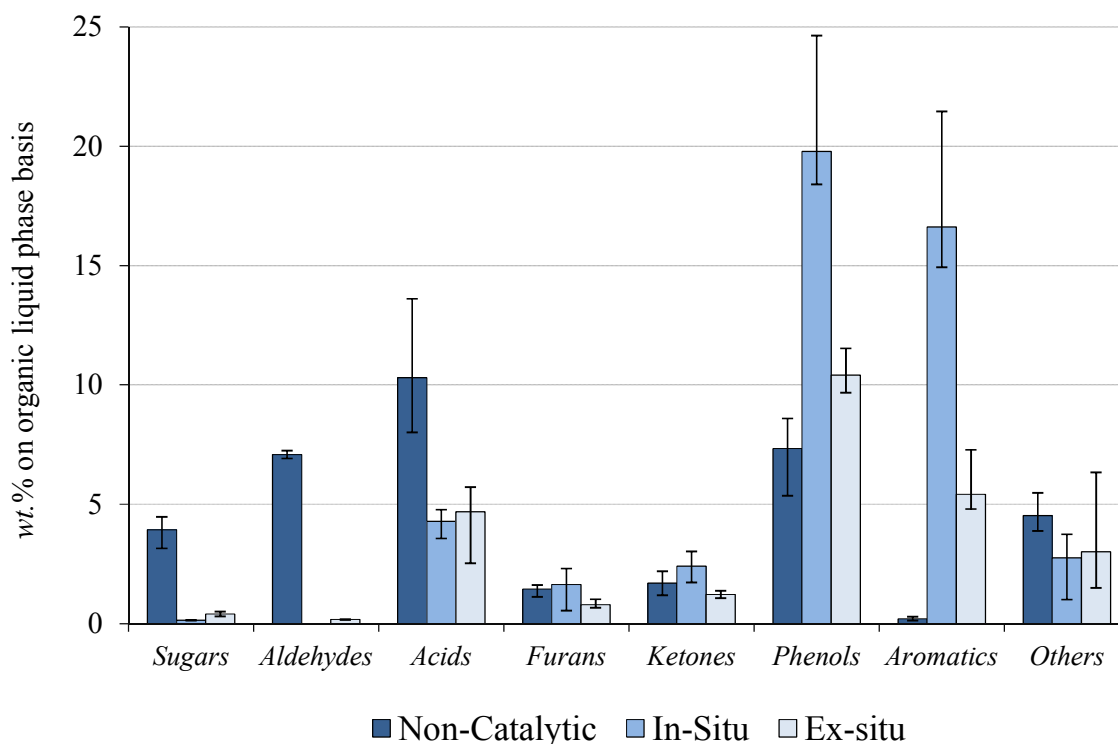


Fig. 3.6. Changes of the functional groups in organic liquid fraction for different experimental modes, as quantified by GC–MS.

The corrosive character of the bio-oil increases with increasing acidity. High acidity makes the bio-oil harder to introduce to engines [141,147], reduces the lifetime of the engine, decreases the stability of the bio-oil, and catalyses polymerization reactions [147,184]. Aldehydes, ketones and sugars also decrease the bio-oil quality by causing ageing reactions [145,147,185]. On the other hand high yields of phenolic compounds and furans is positive because they increase the economical attractiveness of the process and the production of aromatic hydrocarbons makes the liquid product better suitable for fuel production [147,186]. The quality of the bio-oil can be further increased by employing higher catalyst-to-feed ratios [85].

Table 3.6. Changes of the most abundant compounds in organic phase for the different experimental modes, as quantified by GC–MS (wt.% averages on organic phase basis)

	<i>Non-Catalytic</i>	<i>In situ</i>	<i>Ex situ</i>
Identified (total) [wt.% on feed]	19.1	12.6	7.1
(% in total liquid)	(33.3)	(25.1)	(14.2)
<i>Sugars</i>			
Levoglucozan	3.54	0.14	0.41
<i>Aldehydes</i>			
Hydroxyacetaldehyde	3.54	0.00	0.00
<i>Acids</i>			
Acetic acid	7.41	2.93	3.92
Propanoic acid	1.47	0.92	0.53
<i>Furans</i>			
Furfural	0.59	0.00	0.11
<i>Ketones</i>			
2-Cyclopenten-1-one	0.40	1.36	0.65
<i>Phenols</i>			
1,2-Benzenediol	2.43	6.92	3.15
4-Methyl-1,2-benzenediol	1.76	2.79	1.62
4-Ethylcatechol	0.74	1.15	0.69
2,4-Dimethyl-phenol	0.41	1.19	0.66
4-Methyl-phenol	0.36	1.40	0.82
2-Methyl-phenol	0.30	1.19	0.87
Phenol	0.27	2.32	1.24
<i>Monoaromatics</i>			
Xylene (m, p)	0.01	4.67	1.54
Toluene	0.02	2.98	0.62
<i>Diaromatics</i>			
1-Methyl naphthalene	0.02	1.88	0.41
<i>Naphthenoaromatics</i>			
Methyl-1H-Indenes	0.01	1.12	0.55
Indene	0.01	1.10	0.53
Indane	0.01	0.52	0.20
<i>Other</i>			
1-Hydroxy-2-propanone	2.93	1.22	1.42

As can be seen in Fig. 3.6, compounds such as sugars and aldehydes are broken down by the catalyst and a significant decrease of these compounds in the organic fraction was observed. The decrease in some of the key compounds in the virgin bio-oil such as hydroxyacetaldehyde and levoglucozan supports this trend (Table 3.6). There was also a decrease in the acids for catalytic compared against non-catalytic pyrolysis, and in situ catalysis performed better in decreasing the organic acid content. Especially in the in situ experiments, a significant increase in phenol and catechol (1,2-benzenediol) was observed (Table 3.6) while less effect was seen for the ex situ experiment. A possible explanation for this effect is that in in situ mode, the catalyst is able to stabilize part of the vapour phase aromatic monomers derived from lignin decomposition into a phenolic derivative before they

can repolymerize into heavier, hence non GC–detectable, aromatic structures (*i.e.* pyrolytic lignin). Both in in- and ex situ modes, catalysis favoured the production of phenols and aromatics; however, the performance of in situ catalysis was considerably better. There were slight changes in the amount of furans and ketones and the amounts produced by in situ catalysis were higher than that of ex situ catalysis. The use of the catalyst in fast pyrolysis also has a noticeable effect on the quantity of aromatics in the produced bio-oil. With the in situ catalysis, aromatics production of 16.6 wt.% on organic phase basis was determined. This value is more than 80 times higher than the amount of aromatics in the non-catalytic bio-oil. Fig. 3.7 shows the changes of the mono-, di-, and naphtheno-aromatics in organic liquid fraction for different experimental modes. Compared to the non-catalytic mode, clear increases of different aromatic fractions can be observed both in in situ and ex situ catalyst application. The leading group of aromatics was the monoaromatics and the amount of xylene (*m,p*) and toluene reached up to 8 wt.% on organic phase basis in total in in situ mode (Table 3.6).

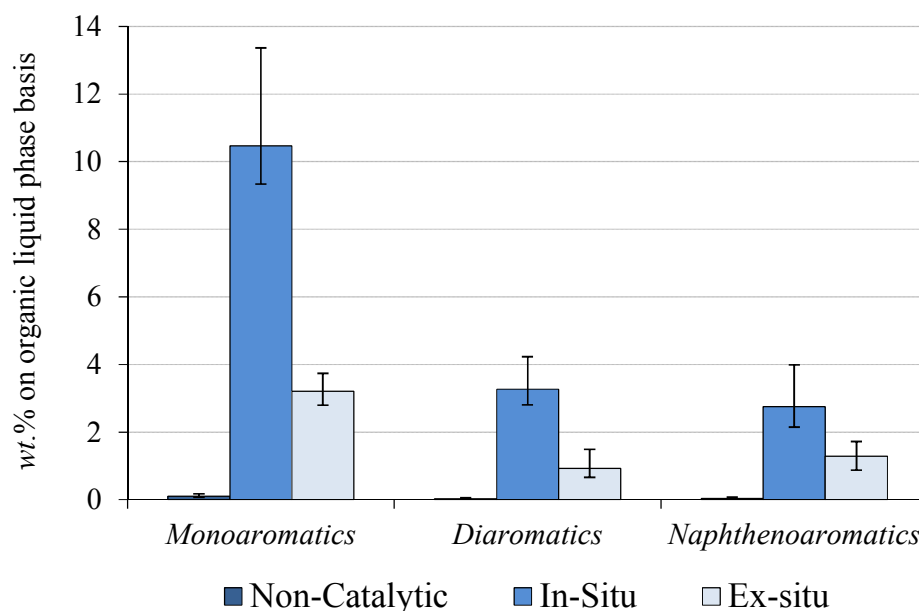


Fig. 3.7. Changes of the mono-, di-, and naphtheno-aromatics in organic liquid fraction for different experimental modes, as quantified by GC–MS.

The total acid number (mg KOH/g liquid (a.r.)) of non-catalytic bio-oil was determined as 102.7. The application of the catalyst decreased this value to 72.1 for in situ and 69.7 for ex situ, respectively. This also supports the decreasing trend in the amount of organic acids shown in Fig. 3.6.

3.3.4 Carbon distribution over the pyrolysis products

From Fig. 3.8, it can be observed that the carbon yield of the catalytic bio-oil is decreased compared to the reference case. Carbon yield in the bio-oil (liquid) is reduced for the catalytic experiments, with ex situ catalysis having a larger reduction in carbon yield than in situ catalysis. For ex situ catalysis, the direct contact of pyrolysis vapours with the catalyst favours the coke deposition on the catalyst surface. As a result of this, the carbon yield of solids (char + system carbon) for the ex situ catalysis case increased. This also supports the conclusions that were drawn above regarding the heat carrier/biomass ratio (Fig. 3.3 and Table 3.4). In combination with Fig. 3.5, it can be concluded that the higher degree of decarbonylation reactions caused an increase in the carbon yield of gases with the presence of catalysts. Also, as can be seen by the total carbon yield, achieving full carbon mass balance closure proved to be difficult which may due to experimental errors in elemental analysis.

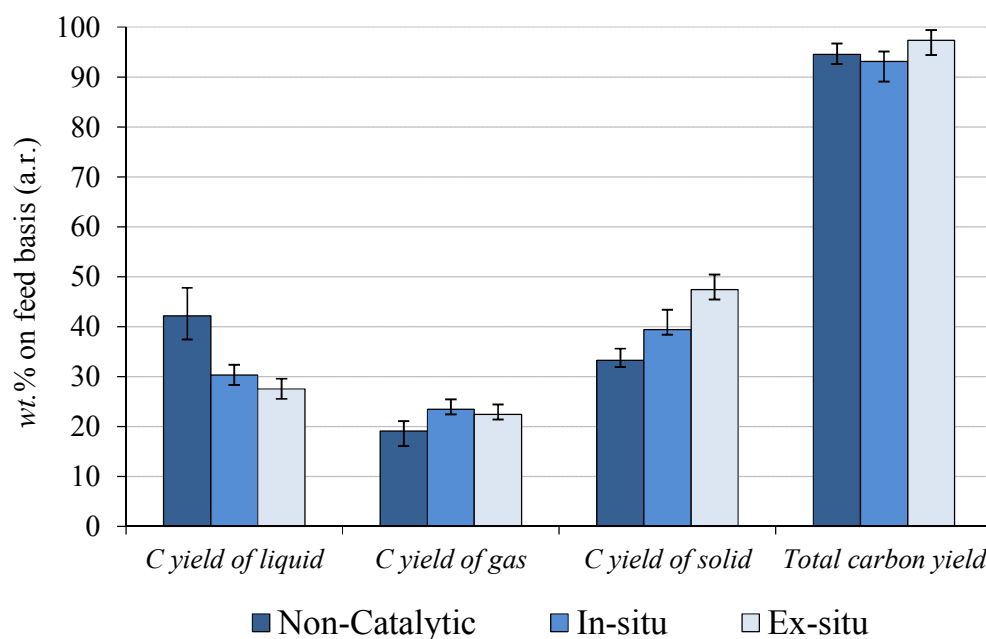


Fig. 3.8. Carbon yields in in situ and ex situ catalytic fast pyrolysis experiments, compared to the reference, non-catalytic experiments.

3.4 Conclusions

Non-catalytic, in situ catalytic and vapour phase upgrading (ex situ) fast pyrolysis of lignocellulosic biomass in a new set-up have been examined in relation to different experimental modes. For the validation of the set-up, several non-catalytic experiments were carried out and the product yields were in-line with literature data for lignocellulosic biomass fast pyrolysis. A heterogeneous ZSM-5 based acidic catalyst was used to observe the effects of the catalyst on the product yields and bio-oil quality, and resulted for both in- and ex situ catalytic pyrolysis experiments in a higher quality bio-oil; this is characterized by the extent of deoxygenation, the production of targeted chemicals (*e.g.* phenols, aromatics), and the elimination of undesired chemicals (*e.g.* aldehydes, acids). However, applying catalysis also

resulted in a significant decrease of the overall liquid yields (50.3 wt.% and 50.1 wt.%, for in- and ex situ respectively) compared to the reference non-catalytic case (58.9 wt.%). In line with this observation higher system carbon yields were observed for the catalytic pyrolysis experiments. The catalytic treatment reduced the oxygen content of the organic phase of bio-oils notably. The conversion of the oxygenated species in the bio-oils was largely due to removal of oxygen in the form of CO, CO₂ and H₂O. Detailed GC×GC–FID and GC×GC–TOF–MS analysis confirmed that the non-catalytic bio-oil was a complex mixture of highly oxygenated, acidic compounds such as acetic acid. The use of in- and ex situ catalysis resulted in a removal of detectable sugars and aldehydes. Also, the concentration of organic acids was decreased while a higher formation of aromatics and phenols was observed in catalytic pyrolysis. Moreover, compared with the in situ mode, ex situ mode consumes less catalyst but the overall performance of in situ catalysis in terms of oil quality is considerably better.

Chapter 4

Screening metal doped catalysts in situ for continuous catalytic fast pyrolysis of pine wood

Abstract

Catalytic fast pyrolysis (CFP) of biomass over metal containing heterogeneous catalysts is a promising route for the production of (partially) deoxygenated liquids suitable for further conversion to fuels and/or chemicals. In this work, pine wood was pyrolyzed catalytically at 500 °C in an auger reactor to investigate the effect of catalyst type on the pyrolysis products. Up to date, in the literature of catalytic fast pyrolysis of woody biomass, mostly ZSM-5 and FCC catalysts were tested in continuously operated setups. In this work, the performances of various other heterogeneous catalysts (metal doped and their parent counterparts) have been examined in a lab-scale unit dedicated for in situ catalytic fast pyrolysis of biomass. In total, eight proprietary catalysts were tested. They were divided into three groups based on their acidity, type of carrier, the active metal they contain, and according to being aged or fresh. The results obtained from catalytic tests have been compared to each other and to non-catalytic control experiments performed with sand. The distribution of products including liquid organics (i.e. CFP-oil), water, char, coke, and non-condensable gases are described as well as the compositions of the liquid organics and non-condensable gases. The presence of catalysts led to the production of additional water, coke and gases at the expense of the liquid organics. However, the quality of the obtained CFP-oil was altered to various degrees depending on the catalyst type. For all catalysts, the acidity of CFP-oils remarkably decreased with an increased deoxygenation. Among all catalysts, the acidic catalyst with lower redox-metal content, and freshly calcined metal doped basic mixed-metal oxide and gamma catalysts were found to be the best performing ones. The catalysts were also tested on a micro-scale using a py-GC/MS system. The py-GC/MS results were found to be only partially indicative for the performance of a catalyst in CFP of biomass.

4.1 Introduction

Lignocellulosic biomass is a renewable resource that contains carbon and hydrogen providing an alternative to fossil fuels. It has also the potential to sustain the chemical economy which is currently largely petroleum-based. Fast pyrolysis of biomass is emerging as a cost effective thermochemical conversion technique that can yield a liquid product (*i.e.* pyrolysis liquid, bio-oil) in high quantities. When the target is to use the pyrolysis liquids in replacing the petroleum fuels its quality needs to be improved. As most of the crude bio-oil's adverse properties are caused by its highly oxygenated nature, bio-oil improvement basically refers to a reduction in the oxygen content (deoxygenation). For this purpose catalytic fast pyrolysis (CFP), which is a single step process that uses heterogeneous catalysts reacting with biomass derived pyrolysis vapours at atmospheric pressure [39], can be put in service.

The possibility to feed a deoxygenated pyrolysis liquid into the existing petroleum refinery infrastructure (*i.e.* blending with VGO prior to the FCC) would make CFP an attractive route for biomass conversion. The presence of the catalysts in CFP induces reactions that involve the removal of the oxygenated species and enhance the cracking reactions of the heavy molecules in primary pyrolysis vapours. With the use of different catalysts, varying degrees of deoxygenation can be achieved via simultaneous decarbonylation (CO rejection), decarboxylation (CO₂ rejection) and dehydration (H₂O forming) reactions [42]. These reactions alleviate the acidity, density, and the viscosity of the pyrolysis liquid and thus increase its stability and calorific value.

In CFP of biomass, the type of the catalyst affects the mechanism of oxygen removal and the spectrum of the produced chemical compounds. The catalyst properties play a vital role in the selectivity towards higher value compounds (alkanes, phenolics, mono-aromatic hydrocarbons, *etc.*) while avoiding undesirable compounds (sugars, acids, poly-aromatic hydrocarbons, *etc.*) [43,44,86]. However, since each catalyst favours different reaction mechanisms, some specific chemicals (*i.e.* aromatics) cannot be produced with every catalyst. Indeed, selectivity can be tuned by changing the physical and/or chemical properties (surface area, pore size, impregnation of active metals, *etc.*) of the specified catalyst or by mixing different catalysts together. Hence, the targeted product specifications determine the selection of the catalyst that serves through the purpose of the CFP operation.

The reported research regarding the development of CFP of biomass spans a wide range of catalyst combinations, temperatures, and feedstocks in an effort to develop fundamental knowledge on the catalytic effects, processes and operating conditions. Apparently, the main goal was to produce a liquid product with less oxygenated compounds and possibly richer in high-value compounds. Large number of studies in the CFP literature has focused on maximizing the production of mono-aromatic hydrocarbons (MAHs). However, the production of aromatics should not be the only criterion that values a catalyst in CFP conditions. Deoxygenation capability, removal of reactive oxygen functionalities, the ability to suppress the formation of coke and PAHs, the activity and lifetime of the catalyst are other parameters that should be considered carefully.

The main objective of this study was to find the best performing catalysts capable of retaining the amount of the organic liquid products as much as possible with a minimum water production, and also achieving an effective reduction of the acidity during in situ CFP of pine wood. In order to determine their individual cracking and deoxygenation performances in in situ fast pyrolysis of pine wood, eight proprietary zeolite catalysts supplied by Albemarle Catalyst Company B.V. (Amsterdam, The Netherlands) were screened. Both a mini-plant based on auger reactor technology and a py-GC/MS system was used while applying the same temperature (500 °C) and catalyst-to-biomass ratio (5). Based on the type of the carrier, their acidity (acidic and basic catalysts), the active metal they contain, and according to the aged/freshly calcined distinction, these catalysts were divided into three groups. The experimental results obtained from in situ application of the catalysts were compared to each other and to the results of non-catalytic experiments which were designated as the base case. The results were investigated based on the obtained product yields (organics, water, char, coke and non-condensable gases), elemental compositions of these product fractions, the acidity and the composition of the pyrolysis liquids (via a GC×GC/MS). The results obtained from py-GC/MS experiments and the use of py-GC/MS in CFP research has been investigated as well.

4.2 Experimental section

4.2.1 Materials

4.2.1.1 Biomass feedstock

Pine wood (Bemap Houtmeel B.V. (Bemmel, Netherlands) was used as the reference biomass feedstock in all experiments. The number-average particle size of pine was between 1 and 2 mm. The moisture and ash content were determined to be 8.4 *wt.*% and 0.3 *wt.*% on a “as-received” basis (a.r.), respectively. For py-GC/MS experiments, the pine wood sample was finely ground in a centrifugal mill and screened to obtain samples with particle sizes of *ca.* 100 µm. The proximate analysis data, elemental composition, alkali metal content and HHV of the pine wood are listed in Table 4.1.

Table 4.1. Properties of pine wood.

Proximate analysis (wt.%)	
Fixed carbon (d.b.)	15.0
Volatiles (d.b.) [ASTM E872-82]	84.8
Moisture (a.r.) [ASTM E871-82]	8.4
Ash (d.b.) [ASTM E1755-01]	0.3
Ultimate analysis (d.b.) [wt.%]	
C	47.1
H	5.9
O	46.4
N	0.04
S	0.06
Alkali metals (d.b.) [mg/kg]	
K	346
Na	10
Mg	113
Ca	767
HHV (a.r.) [MJ/kg] [†]	16.8
HHV (d.b.) [MJ/kg]	18.3

[†] Calculated by using the Milne formula [187]

4.2.1.2 Catalysts

Eight proprietary catalysts were used to investigate their impact on pyrolysis product distribution. The catalysts supplied by Albemarle Catalysts Company B.V. (Amsterdam, The Netherlands) were provided in powdered form. To minimize the water accumulation in the final liquid product, most catalysts were calcined in air at 500 °C for 1 hour before shipment to decrease the catalyst bound/absorbed moisture content to below 1 wt., after which they have been packaged under inert conditions; with the exception of the catalysts labelled with the suffix “-A”, which had been calcined and subsequently stored for five months to study the effect of aging on the catalyst. Here, the term ‘aging’ represents the anticipated adsorption of water and/or CO₂ on the catalyst from its contact with air. Physical and chemical properties of the catalysts used can be found in Appendix A (this appendix is confidential and can only be accessed by signing a confidentiality agreement).

The first group of (three) catalysts are all based on an acidic zeolite (ZSM-5) containing material and have been labelled “A” for acidic. Two major catalyst variations were made, both containing a not-further-specified redox metal M1. The first modification, termed A-M1-H, contained a high amount of redox metal M1. The second modified version had a lower metal content and lower zeolite content. This catalyst has been labelled A-M1-L. The catalysts in this group contain varying amounts of ZSM-5 in their structure, *viz.* 40 wt.% in catalyst A and 28 wt.% in A-M1’s. The M1 metal content for the low metals version is more than five times lower than the high metals version. This variation in metal content had no measurable effect on the total surface area, but selective pore blocking cannot be excluded. As

a result of the loading of redox metal M1 on the particles (typically 90 μm in diameter), the averaged diameter increased significantly for both “-H” and “-L” variants.

The three catalysts of Group 2 were based on the same basic material, denoted as “B”. Catalyst B is known for its hygroscopic nature and had a much higher loss-on-ignition (L.O.I.) compared to other catalyst after prolonged exposure to (moist) air. On this basic material B, the metal M2 has been added in a similar amount as M1-L. The obtained catalyst is named B-M2. As being the same catalyst, the difference between B-M2-A and B-M2-F is the aged and fresh distinction. After being synthesized, B-M2 was calcined and stored. After 5 months, half of the B-M2 was taken and calcined one more time and named as B-M2-F (fresh). The remaining aged part was then labelled as B-M2-A. Due to the loading with metal M2, the (BET) surface area of the particles halved compared to the original B catalyst.

The last group of catalyst was prepared from a γ -alumina material and subsequently labelled as “G”. This catalyst also contained the metal M2 as used in the basic catalyst B-M2 in the same amount, and distinction was made between aged material G-M2-A and freshly calcined G-M2-F.

Prior to each mini-plant experiment, catalysts were blended with silica sand (PTB-Compaktuna, Gent, Belgium) with a mean diameter of 250 μm and a particle density of 2650 kg/m^3 (compacted bulk density = 1660 kg/m^3).

4.2.2 Experimental setups

4.2.2.1 Fast pyrolysis mini-plant

Catalytic fast pyrolysis experiments were performed in a fully controlled, continuously operated bench scale mini-plant designed and constructed by Biomass Technology Group B.V., BTG (Enschede, The Netherlands) based on auger reactor technology. This mini-plant (Fig. 4.1) has a maximum biomass throughput of 500 $\text{g}\cdot\text{h}^{-1}$ and enables three types of biomass fast pyrolysis experiments *viz.* non-catalytic (using hot sand as the heat carrier), in-situ catalytic (using mixtures of sand and catalyst as heat carrier) and ex-situ catalytic (vapour phase upgrading) [100]. In this study, only in-situ catalytic fast pyrolysis experiments were performed to test various zeolite catalysts. Results obtained for each individual catalyst type were compared with each other, and with the previously published non-catalytic data [100] (Chapter 3 in this thesis). This mini-plant has been described extensively in an earlier publication [100].

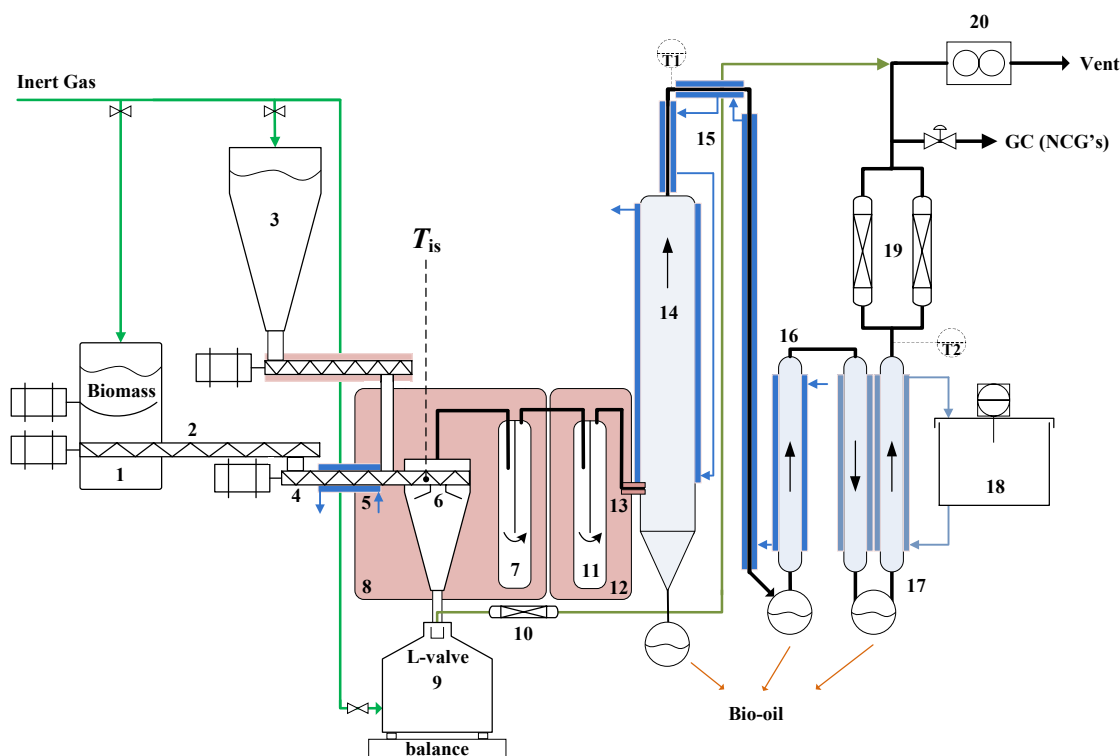


Fig. 4.1. Scheme of the pyrolysis mini-plant: (1) biomass storage hopper; (2) biomass feeding screw; (3) heat carrier storage hopper; (4) auger screw; (5) cooling jacket; (6) in-situ reactor; (7) knock-out vessel; (8) in-situ reactor oven; (9) solids collection vessel; (10) gas filter; (11) secondary knock-out vessel; (12) secondary oven; (13) condenser inlet heater; (14) cold trap condenser tower; (15) tap water cooled stainless steel pipelines; (16) tap water cooled spiral glass condenser; (17) ethylene glycol cooled spiral glass condensers; (18) refrigerated cooler; (19) cotton filters; and (20) gas flow indicator. Green: N₂ lines; pink: heated zones; blue: cooled zones.

An integrated screw feeder system, consisting of a biomass storage hopper with a capacity of 4 kg (*no.* 1) and a biomass feeding screw (*no.* 2), is used to transport the biomass to the auger screw (*no.* 4). The variable turning frequency of the biomass feeding screw enables feed flow rates from 0.1 to 0.5 kg. In this work, a constant biomass flow rate of 0.2 kg/h was used for all experiments which yielded *ca.* 0.1 kg/h of pyrolysis liquid, suitable for a full characterization.

The last section of the auger screw serves as the biomass fast pyrolysis reactor that is from the point where the biomass and heat carrier are intensively mixed. The solid material's residence time is *ca.* 1 s (*no.* 6). The temperature in this section is taken to be the in situ reactor temperature, T_{is} . This temperature is used as the set point for the ovens' (*no.* 8 and *no.* 12) (Westeneng Ovenbouw B.V.) control loop. To prevent biomass decomposition before contact with the heat carrier, a water-cooled stainless steel jacket (*no.* 5) was placed around the front section of the auger. The heat carrier is transported to the auger screw through a 110 cm long heated screw from the heat carrier storage hopper with a storage capacity of 25 kg (*no.* 3).

While the produced vapours are entrained to the knock-out vessels (*no.* 7 and *no.* 11) by the continuous inert gas flow (N_2), the solid particles (char, sand, catalyst) fall down to the solids collection vessel (*no.* 9). In order to assure complete devolatilization of the biomass particles, an L-valve type of solids buffer is placed in the entrance of the collection vessel. This valve is a bent pipeline that slows down the solids flow and allows an additional solid hold-up to extend the contact time of charred biomass with the hot heat carrier.

Pyrolysis vapours flows through the condenser via a heated inlet line that prevents local tar accumulation (*no.* 13). The condensation of the pyrolysis vapours into the pyrolysis liquid takes place in a tap-water cooled condenser system which is composed of a condenser tower (*no.* 14), vapour transfer pipelines (*no.* 15), and a spiral glass condenser (*no.* 16). To maximize the liquid collection, the outgoing gas stream finally passes through two ethylene glycol cooled spiral glass condensers (*no.* 17) which are operated at $-25\text{ }^{\circ}\text{C}$ and cotton filters (*no.* 19). The volumetric flow rate of the outgoing non-condensable gases is measured with a dry gas flow indicator (Itron, Gallus 2000 G1.6, accuracy is 10^{-4} Nm^3) (*no.* 20). Several thermocouples and pressure sensors are placed along the setup to continuously monitor the temperature and pressure at various points. The mini plant unit was fully automated by using industrial system software (Advantech ADAMView).

The possible ranges of the most significant operating parameters and the experimental procedures are listed in an earlier publication [100]. In all in situ CFP experiments, the catalyst samples were mixed with sand in a mass ratio of 1:6.67. The quantities of catalyst and biomass used were *ca.* 1 and 0.2 kg, respectively, resulting in a catalyst to biomass mass ratio of *ca.* 5. All in situ catalytic fast pyrolysis experiments were carried out at a fixed reactor temperature of $500\text{ }^{\circ}\text{C}$ for an experimental run time of 60 min. Inert gas flow rates were kept constant at 120 L/h.

4.2.2.1.1 Mini-plant CFP product analysis

The composition of non-condensable gases was determined off-line using a micro GC (Varian 490-GC) equipped with two TCD detectors and two analytical columns. Helium and Argon (Alphagaz) were used as carrier gases. The first column (10 m Molesieve 5A (with backflush)) was set at $75\text{ }^{\circ}\text{C}$ to determine H_2 , inert N_2 , CH_4 and CO . The second column (10 m PPQ) was set to $70\text{ }^{\circ}\text{C}$ and used for the determination of CO_2 , C_2H_4 , C_2H_6 , C_3H_6 and C_3H_8 . The sum of C_2H_4 , C_2H_6 , C_3H_6 and C_3H_8 is referred to as C_{2+} . This GC was calibrated prior to each experiment by using two different gas mixtures of a known composition. The total volume of the outlet gas mixture is measured using a gas flow indicator (in Nm^3 , accuracy is 10^{-4} Nm^3). To determine the exact volume percentage of each individual gas component in the non-condensable gas mixture, the molar amount of each gas was calculated by the ideal gas law.

The amount of char was determined by means of sieving the contents of the solids collection vessel. Small amounts of char were taken for the elemental analysis which was carried out with a Thermo Scientific Flash 2000 Organic Elemental Analyser. The amount of system deposits (*i.e.* solid carbonaceous matter other than char) was determined by subjecting the char-free content of the solids collection vessel to combustion in air using a muffle furnace (Carbolite AAF 1100) at 600 °C for 6 h. In the case of non-catalytic experiments, an average system deposits value of *ca.* 3 wt.% was obtained (checked a number of times). The amount of coke in the case of catalytic experiments was determined by applying the same procedure. The coke yield was then simply calculated by subtracting the average non-catalytic system deposits value from the average catalytic system deposits value.

At the end of each experiment, the whole cold-trap condenser system was flushed with tetrahydrofuran (THF). The use of this solvent allowed the complete collection of the heavy bio-oil fractions that are stuck on the condenser walls and in the vapour pipelines. The collected bio-oil/THF mixture (single phase) was later analysed via a GC×GC–FID in terms of its THF content to determine its dilution factor. The detailed characterizations of bio-oils were performed on a GC×GC setup which is a combination of GC×GC–FID and GC×GC–TOF–MS [50,180]. This setup is equipped with two columns (Rtx-1 PONA (50 m L × 0.25 mm I.D. × 0.5 µm df) and BPX-50 (2 m L × 0.15 mm I.D. × 0.15 µm df)) and both an FID and a TEMPUS TOF-MS (Thermo Scientific, Interscience Belgium) detectors. Dibutyl ether and fluoranthene were used as internal standards. The injection volume was 0.2 µl, with a split flow of 150 ml/min, and an injector temperature of 280 °C. Identification of the compounds was done based on the retention time.

The water content of bio-oils was determined by Karl Fischer Titration (Mettler Toledo V20 with 5 ml burette; electrode: DM 143-SC; reagent: Merck Combi Titrant 5 Keto; solvent: Merck Combi Solvent 5 Keto). The acidity of the oil samples was identified in terms of TAN (total acid number, in mg KOH/g liquid) (Metrohm 848 Titrino-Plus; titrant: KOH, 0.1N; solvent: propan-2-ol and toluene, combined glass (pH) electrode, incorporated reference system LiCl saturated in ethanol).

To obtain a good estimation of experimental errors, all the CFP experiments and product analyses were performed in duplicates and in triplicates, respectively. All the values presented in this work are averaged. For any detailed information regarding the yield calculations and further experimental procedures, the reader is directed to our earlier publication [100].

4.2.2.2 Py-GC/MS system

Catalytic fast pyrolysis experiments were performed in situ by using a micro-pyrolysis unit (Multi-shot pyrolyzer EGA/PY-3030D, Frontier Laboratories Ltd., Fukushima, Japan) coupled to a Thermo Trace GC Ultra gas chromatograph (GC) with an ISQ mass spectrometer (MS) detector. About 0.5 mg of pine was put to a sample cup made of deactivated stainless steel (Frontier Laboratories Eco-cup, 80 μ l). For the in situ experiments, the amount of catalyst used was *ca.* 2.5 mg to obtain a catalyst/biomass ratio of 5 (*wt./wt.*) which was the same as in mini-plant experiments. The catalyst and the pine particles were physically mixed in these defined proportions and a layer of quartz wool was placed on top of catalyst/pine wood mixture to hold it in the cup during pyrolysis. The loaded sample cup was dropped instantly by gravity into the quartz tube situated inside the preheated furnace. Consequently, the sample was heated rapidly to the desired pyrolysis temperature of 500 °C at a heating rate of *ca.* 2000 °C/s (this heating rate is claimed by the manufacturer). Released pyrolysis vapours were swept from the open end of the quartz tube into the pyrolysis interface (kept at 350 °C) with a helium carrier gas stream (Air Liquide, Herenthout, Belgium, purity: \geq 99.9%) and then routed to the GC-MS system.

The pyrolysis vapours are directly injected into the GC using a split/splitless injection port (split ratio 1:100) operated at 300 °C. The chromatographic separation of pyrolysis products is performed using a Restek capillary column (Rtx-1707, 60m L x 0.25 mm I.D. x 0.25 μ m df) with a stationary phase consisting of a crossbound 14 % cyanopropylphenyl and 86 % dimethyl polysiloxane and a constant helium carrier gas flow of 1 ml/min. The GC oven temperature program started with a 3 min hold at 40 °C followed by heating to 280 °C at 5 °C/min. The final temperature was held constant for 1 min.

Subsequent to the separation in the GC column, pyrolysis compounds were identified by using an MS. The integration and identification of chromatographic peaks were performed by system software (Xcalibur 2.1). Each peak appearing in the obtained mass spectra was interpreted using the NIST08 library. Three identical experimental runs were carried out per sample and the obtained data were averaged.

4.3 Results and discussions

4.3.1 In situ catalytic fast pyrolysis – Mini-plant results

4.3.1.1 Product yields

The amounts of the organics, water, char (in combination with system deposits), coke on catalyst, and non-condensable gases were determined experimentally, allowing for the determination of the overall mass balance for the CFP process. The results are shown in Fig. 4.2. Mass balance closure varied between 96.0 *wt.*% and 102.9 *wt.*%. Small but inevitable product losses, which are inherently related to this scale of operation, are the reason that the mass balances could not be closed completely. Variations were mainly due to the handling, collection and weighing of the products. The experimental reproducibility showed a standard deviation of each product below 8%, indicating accuracy sufficient for observing trends in the experiments.

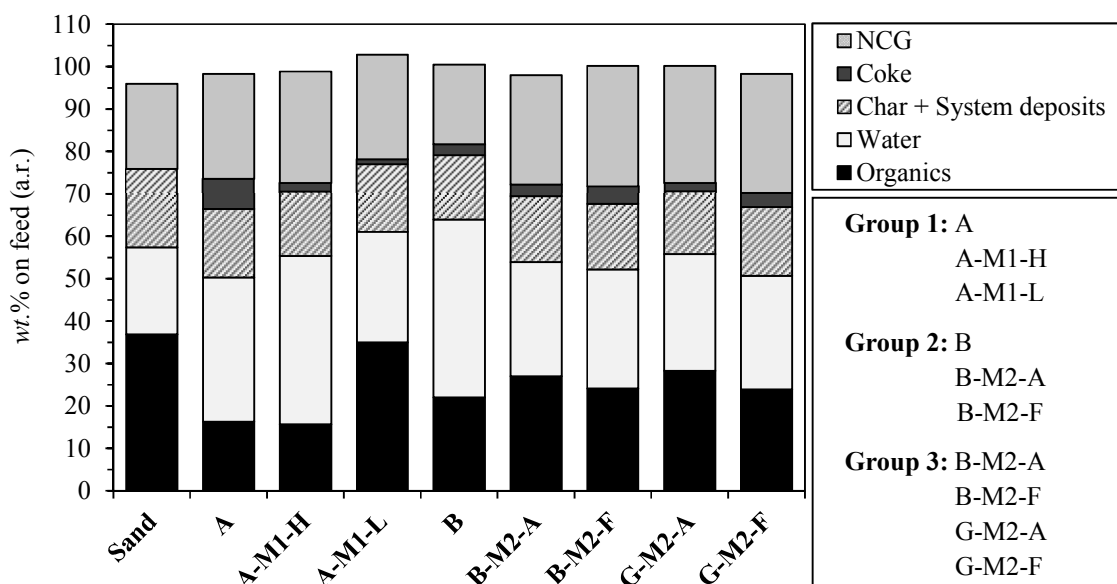


Fig. 4.2. Mass balances for fast pyrolysis of pine wood in the presence of various catalysts. The first bar shows the result of the non-catalytic (sand) experiment. All experiments were performed at a reactor temperature of 500 °C.

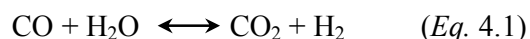
In the tests with Group 1 catalysts, compared to the non-catalytic value of 36.9 wt.%, the smallest decrease in organics yield was seen with A-M1-L which yielded 35.0 wt.% of organics. Although catalysts A and A-M1-H gave almost the same yield in organics, the difference between these two catalysts were observed as higher water and lower coke yields found with A-M1-H. Group 1 catalysts contain varying amounts of ZSM-5 in their structure (40 wt.% in catalyst A and 28 wt.% in A-M1's). ZSM-5 is an active cracking and deoxygenating catalyst which is widely used in the research dealing with catalytic deoxygenation of biomass fast pyrolysis liquids and vapours. Its high activity results in low yields of hydrocarbons and high yields of coke and water [69]. In general, when different types of porous catalysts are involved in CFP of biomass, the production of water, coke and non-condensable gases (NCG) is favoured at the expense of organics [72]. The lower yield of organics is an indication of a higher degree of cracking and deoxygenation. As expected, water, NCG and coke yields increased with both catalysts, except A-M1-L; it showed a performance with the smallest increases in the aforementioned products. The reason for the high water yield (39.7 wt.%) obtained with A-M1-H is likely due to the higher redox metal content in this catalyst which caused additional water production (a detailed explanation can be found in Appendix B. This appendix is confidential and can only be accessed by signing a confidentiality agreement). Adversely, the lowest water yield in this group was obtained with A-M1-L (26.1 wt.%), which was even lower than that of catalyst A (34.0 wt.%), revealed that the lower amount of redox metal in this catalyst suppresses the formation of water. Overall, it can be concluded that the variation of the metal content in a ZSM-5 catalyst can significantly change the product distribution in CFP of biomass.

The primary fast pyrolysis vapours from pine underwent various reactions in the presence of catalysts, including deoxygenation reactions (dehydration, decarboxylation, decarbonylation) that resulted in the production of hydrocarbons, but also in additional heterogeneous coke. Compared to the char yield obtained in non-catalytic experiments, the amount of char produced decreased in similar quantities (*ca.* 3 wt.% on feed basis, a.r.) with all catalysts tested in this work which revealed that the presence of zeolite catalysts promote the biomass devolatilization. This may be caused by higher biomass particle heating rates in the presence of catalysts, due to a reduction in the average particle diameter of the heat carrier (*i.e.* sand-catalyst mixture). The reason for the similar char yields in the presence of catalysts was due to the fact that each catalytic experiment has been carried out under identical process conditions (reaction temperature, catalyst-to-sand ratio, catalyst-to-biomass ratio, biomass residence time and heating rate).

In general, a larger coke production is observed for the catalysts that also show higher yields of aromatics. This may be related to their dehydration activity (see Table 4.2). The highest coke yield (7.1 wt.%) was seen for catalyst A. The presence of the redox metal in ZSM-5 suppressed the coke production by 2.1 wt.% and 1.2 wt.%, for A-M1-H and A-M1-L, respectively. A higher hydrogen partial pressure (due to water-gas shift reaction) could promote hydrogenation and limit the dehydrogenation. This low coking rate of the redox metal was in line with the observations found in the literature [110].

With Group 1 type catalysts, increases in non-condensable gas yields were observed compared to the non-catalytic experiments which had a non-condensable gas yield of 20.5 wt.%. Although the differences between catalyst A and its redox metal containing counterparts were small, it can be concluded that, on average, high weight percentage redox metal containing A-M1-H gave the highest yield of NCG's with a yield of 26.3 wt.%, which is 1.6 wt.% higher than that of A-M1-L. This revealed that, the increase of redox metal in the catalysts promotes gas production. It should also be noted that although the amount of ZSM-5 (cracking catalyst) is lower in A-M1 catalysts (40 wt.% in catalyst A and 28 wt.% in A-M1's), the larger NCG yields in A-M1-H and in A-M1-L compared to that of catalyst A, further shows the promotion of gas products by the presence of redox metal in the catalyst.

Compared to the non-catalytic yields, the yields of water, coke and NCG's increased with the presence of Group 2 type catalysts at the expense of organics and char. The only exception was the lower NCG yield (18.8 wt.%) found with the catalyst B. In general, basic mixed-metal oxide catalysts favour the dehydration mechanism while suppressing the decarbonylation and decarboxylation mechanisms (see Fig. 4.2 and Fig.4.3). The very high water yield observed in the presence of basic catalyst B (42.0 wt.%), revealed that the main deoxygenation mechanism with this catalyst was dehydration. The addition of the metal M2 on catalyst B (*i.e.* B-M2-A and B-M2-F) decreased the water yields but boosted NCG yields, showing that the presence of metal M2 promotes the production of gases rather than the dehydration mechanism. Specifically, metal M2 shifts the water-gas shift reaction (Eq. 4.1) to the right (see Appendix B), favouring CO₂+H₂ production over CO₂ consumption (see Fig. 4.3).



When aged (B–M2–A) and freshly calcined (B–M2–F) catalysts are compared, the effect of calcination was observed as small increases in water, coke and NCG yields and a slight decrease in the organic yield observed in case of the freshly calcined counterpart. It simply confirms that the freshly calcined catalysts are slightly more active, they promote deoxygenation (more water and more gas) thereby increasing the amount of coke and coke precursors.

Comparing Group 3 catalysts, the effects of the various catalysts are relatively small. If compared to the non-catalytic case, the water, coke and NCG yields increased again at the expense of organics and char yields. Although the presence of metal M2 on different carriers (B and G) did not show any remarkable effects on the yields, the aged/freshly calcined comparison reveals obvious differences. The NCG and coke yields obtained from freshly calcined catalysts (B–M2–F and G–M2–F) were larger than those from their aged counterparts (B–M2–A and G–M2–A). This was because of the carbon which was supposed to be converted/reacted to form liquid products stayed in the catalyst pores as coke or might be due to the selective blocking (by either water or CO₂) of the active sites and/or pores. Moreover, aged catalysts yielded slightly more organics than the freshly calcined ones which also points at a reduced catalytic activity (*i.e.* more oxygenated organics). The water and char yields were quite similar in both catalysts. Although the differences in product distributions are very small with Group 3 type of catalysts, detailed gas, liquid, and elemental analyses in the following sections will reveal some other differences between them.

4.3.1.2 Non-condensable gas analysis

Total non-condensable gas yields including the yields of individual gas compounds and the dimensionless CO/CO₂ ratios are shown in Fig. 4.3. Production of water and CO_x compounds (CO and CO₂) is an indicator of the deoxygenation capability of a catalyst in CFP of biomass.

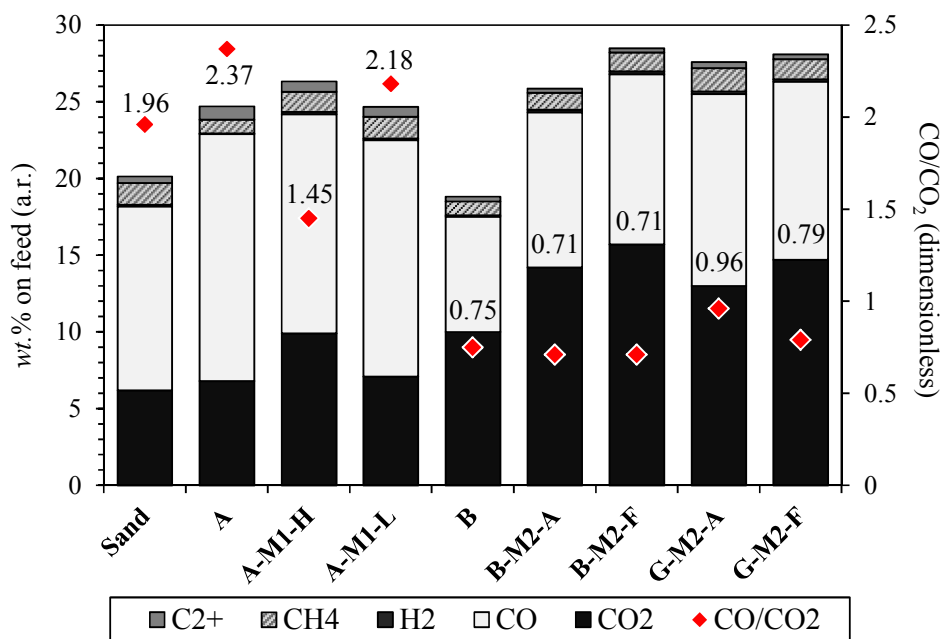


Fig. 4.3. Non-condensable gas composition and dimensionless CO/CO₂ ratios (♦) resulting from fast pyrolysis of pine wood in the presence of various catalysts, compared to the reference, non-catalytic (sand) experiments. The numerical values of the CO/CO₂ ratios are included. All experiments were performed at a reactor temperature of 500 °C.

When observing the changes in CO and CO₂ yields, it can be concluded that, compared to non-catalytic results, Group 1 type catalysts seem to favour decarbonylation (CO production) reactions while Group 2 and Group 3 type catalysts favour decarboxylation (CO₂ production) reactions. However, it should be noted that the change in CO/CO₂ ratio could also be partly or entirely caused by water-gas shift reaction induced by the (redox) metal loading. Among the tested catalysts, catalyst A gave the highest yields of CO with 16.1 wt.%. This yield was 14.3 wt.% for A-M1-H and 15.4 wt.% for A-M1-L (see Appendix B). On the other hand, an increased CO₂ production from 6.8 wt.% with catalyst A to 9.9 wt.% for A-M1-H, and 7.1 wt.% for A-M1-L was observed. In line with the decrease of CO and the increase in CO₂, the increase in H₂ was related to the promotion of water-gas shift reaction (Eq. 4.1). H₂ yield of 0.04 wt.% observed with catalyst A increased to 0.15 wt.% for A-M1-H and 0.11 wt.% for A-M1-L. This may be due to the consumption of hydrogen atoms for the production of aromatic hydrocarbons (see Table 4.2). This is supported by the decrease in the non-catalytic CH₄ yield from 1.4 wt.% to 0.9 wt.% in the presence of catalyst A.

With Group 2 catalysts, the lowest CO and CO₂ yields were found with catalyst B with 7.5 wt.% and 10 wt.%, respectively. Together with the high water yield shown in Fig. 4.2, these results revealed that catalyst B promotes dehydration while water-gas shift is not caused significantly by this catalyst. The presence of metal M2 promoted the increase in CO₂ and H₂ yields which is an indication of the effect of M2 on the water-gas shift reaction (Eq. 4.1). Slight decreases in CO/CO₂ ratio from 0.75 for catalyst B to 0.71 for catalysts B-M2-A and B-M2-F supports this statement. The increased yield of H₂O (compared to the non-catalytic case) and the decreased yield of CO₂ were favourable for moving the reaction to the right-hand side of this equilibrium, resulting in the depletion of CO and the formation of H₂.

However, with the M2 containing catalysts (Group 3), the amount of CO produced was still higher than that of catalyst B revealing that the presence of M2 also promotes CO production (decarbonylation) and not all of it was reacted in water-gas shift reactions. Moreover, freshly calcined B–M2–F catalyst gave higher NCG yields compared to that of aged B–M2–A.

When Group 3 catalysts were considered, the gaseous product yields were quite similar to each other revealing that type of active metal (M2) the catalyst contains is decisive.

When the CO_x (sum of CO and CO₂) is considered (Fig. 4.3), the highest and lowest yields were seen in B–M2–F with 26.8 wt.% and in catalyst B with 17.5 wt.%, respectively. The CO_x yield of catalyst B was even lower than that of non-catalytic value due to the fact that this catalyst favours dehydration (H₂O production) reactions rather than decarbonylation and decarboxylation reactions. The presence of metal M2 boosted the production of CO_x and freshly calcined catalysts yielded more CO_x compared to their aged counterparts. The higher yield of CO_x found with A–M1–H (24.2 wt.%) revealed that higher wt.% redox metal favoured the deoxygenation through CO_x more than that of lower wt.% redox metal containing A–M1–L which gave a CO_x yield of 22.5 wt.%.

4.3.1.3 Deoxygenation performances of the catalysts

The target of a CFP process should be to produce a maximum amount of liquid organics (CFP-oil), while minimizing the oxygen content of it and keeping its H/C ratio as much as possible. CO_x and H₂O yields can be considered as the indicators of the deoxygenation performances of various catalysts. On the other hand, higher H/C and lower O/C ratios are preferable in terms of the energy content of the produced pyrolysis liquid. To this end, decarboxylation is more advantageous than dehydration because it minimizes the loss of hydrogen which is important for the catalyzed hydrocarbon forming reactions. Moreover, compared to decarbonylation wherein a single oxygen atom is removed per carbon atom, decarboxylation maximizes oxygen removal with minimal carbon loss (two oxygen atoms per carbon atom) and thus allows maintaining high H/C ratio and low O/C ratio for the bio-oil [100,177]. A useful representation for gaining insight into the effects of catalysts and process conditions on the elemental composition of the CFP-oil is a van Krevelen plot [188]. The results are provided in Fig. 4.4. Moreover, Fig. 4.5 shows the yields and oxygen contents (both on a dry basis) of the organics fraction of the fast pyrolysis liquids produced over various catalysts. This figure is meant to show the best performing catalysts with respect to the production of the highest yield of organic fraction with the least oxygen content.

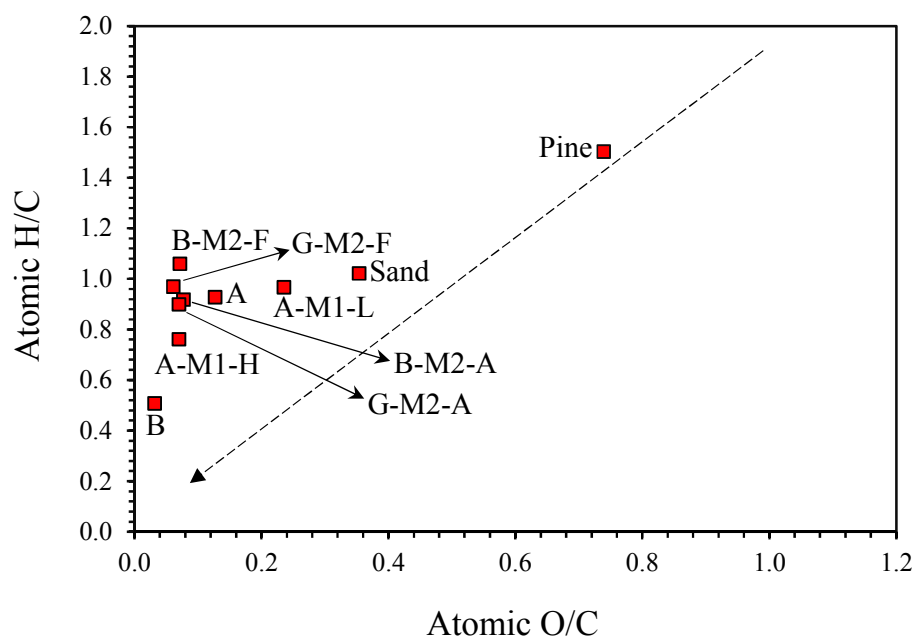


Fig. 4.4. van Krevelen plot for the organics fractions of the fast pyrolysis liquids (dry basis) produced in the presence various catalysts. The reference data points, belonging to the non-catalytic (sand) experiment and biomass feedstock (pine wood) have been added for comparison. All experiments were performed at a reactor temperature of 500 °C. The dashed line represents the dehydration line.

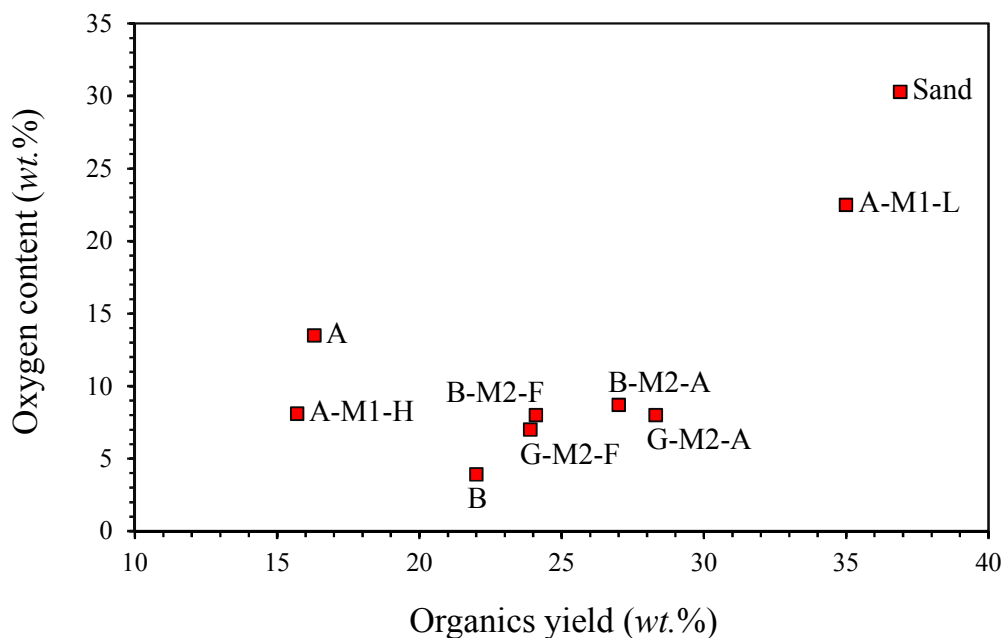


Fig. 4.5. Oxygen contents of the organics fraction of the fast pyrolysis liquids produced over various catalysts plotted versus the organics yield. The reference, non-catalytic (sand) data point has been added for comparison. All experiments were performed at a reactor temperature of 500 °C.

In this work, all CFP-oils show lower oxygen contents compared to that of non-catalytic pyrolysis liquid revealing that all catalysts tested in this work deoxygenated the organic fraction to various extents. These findings (particularly the O/C ratio shown in Fig. 4.4) are in a similar range as reported for the hydrotreated bio-oils under deep HDO conditions [189]. A remarkable result is seen for catalyst B. It produced no more CO_x than the non-catalytic base case (see Fig. 4.3), while at the same time produced the highest amount of water (see Fig. 4.2). Fig. 4.4 and Fig. 4.5 also confirm that the CFP-oil produced with catalyst B is a low oxygen containing, carbon-rich oil. Compared to the non-catalytic value of 19.1 % (relative % to feed), the carbon content of all catalytically produced gases increased except for catalyst B; it gave a (lower) value of 15.6 %. Obviously, in case of catalyst B, the deoxygenation takes place largely by dehydration (see Table A.4.1 in the Supporting Information). For B-M2-A and B-M2-F, the presence of metal M2 increased the atomic H/C ratio (evidence of the presence of hydrocarbons) while keeping the atomic O/C ratio at a level very close to that of catalyst B.

Although the highest quantity of CFP-oil was obtained with low concentration redox metal containing A-M1-L, it also has the highest oxygen content (22.5 wt.%). The addition of a lower amount of redox metal to catalyst A seems to be beneficial for maintaining the oil yield but not for the oxygen removal. On the other hand, higher concentration redox metal containing A-M1-H catalyst remarkably decreased the oxygen content in the oil; however, it produced the lowest amount of CFP-oil among other catalysts. Based on the results in Fig. 4.4 and Fig. 4.5, one would conclude that metal M2 containing basic and γ -alumina catalysts (Group 3) showed good performances. Especially the aged versions B-M2-A and G-M2-A, came forward with their fairly low oxygen content and high oil yields. Moreover, the oxygen content of gaseous products increased for both catalysts (Table A.4.1 in the Supporting Information), especially for Group 3 type catalysts this increase was more pronounced. These results supported the increases in the yields of CO and CO_2 and revealed that deoxygenation through gaseous products (instead of water) were favoured in the presence of these catalysts (with an exception of catalyst B). The LHV values of gases varied from 10.7 MJ/m³ to 15.4 MJ/m³ which are in the range of the medium level gaseous fuels. These gases could be used directly in engines, turbines and boilers for power production [190] (see Table A.4.2 in the Supporting Information).

4.3.1.4 Acidity: results of TAN measurements

One of the main objectives of catalytic fast pyrolysis is to enable a feed suitable for oil refineries. The physical and chemical properties of the CFP-oils must be closer to the typical hydrocarbon feed than the virgin bio-oil. The determination of the total acid number (TAN) is a basic and a preferred method for measuring the acidity of hydrocarbons [191]. The TAN of non-catalytic bio-oil is around 100 [192] and this value is supposed to drop by CFP. The acidity of bio-oil is mainly due to volatile organic acids like acetic and formic acid, and the total acid number of bio-oil measured by titration was shown to correlate highly with the organic acid concentration measured by GC/MS [193]. On the other hand, phenolic compounds also contribute to the acidity of bio-oil (phenol, $\text{pK}_a=10$, acetic acid, $\text{pK}_a=4.8$), but to a much lesser extent [177]. An increase in the yield of CO_2 during CFP can be related

to the deoxygenation of carboxylic acids and thus to a decreased acidity in the produced bio-oil. Fig. 4.6 shows TAN and the dimensionless CO/CO₂ values for in situ catalytic fast pyrolysis of three different groups of catalysts, compared to the reference, non-catalytic (sand) experiments of pine wood at 500 °C. The lower values of CO/CO₂ ratio (see Fig. 4.3) indicate a preference for decarboxylation reactions over decarbonylation ones, and then lower TAN values are expected. Among all the catalysts, catalyst B showed the lowest TAN value (3.8 mg KOH/g pyrolysis liquid) which is an indication of the effective removal of carboxylic acids (see Table 4.2). The presence of metal M2 increased the TAN but a difference between aged and freshly calcined B–M2 catalyst is not observed. Similarly, with G–M2 catalysts, the TAN values were almost the same while here the freshly calcined G–M2–F gave a slightly smaller value for the CO/CO₂ ratio (indication of favoured decarboxylation reactions with this catalyst). Group 1 type catalysts showed a consistent correlation between the TAN and CO/CO₂ ratio; with increased CO₂ production TAN decreased.

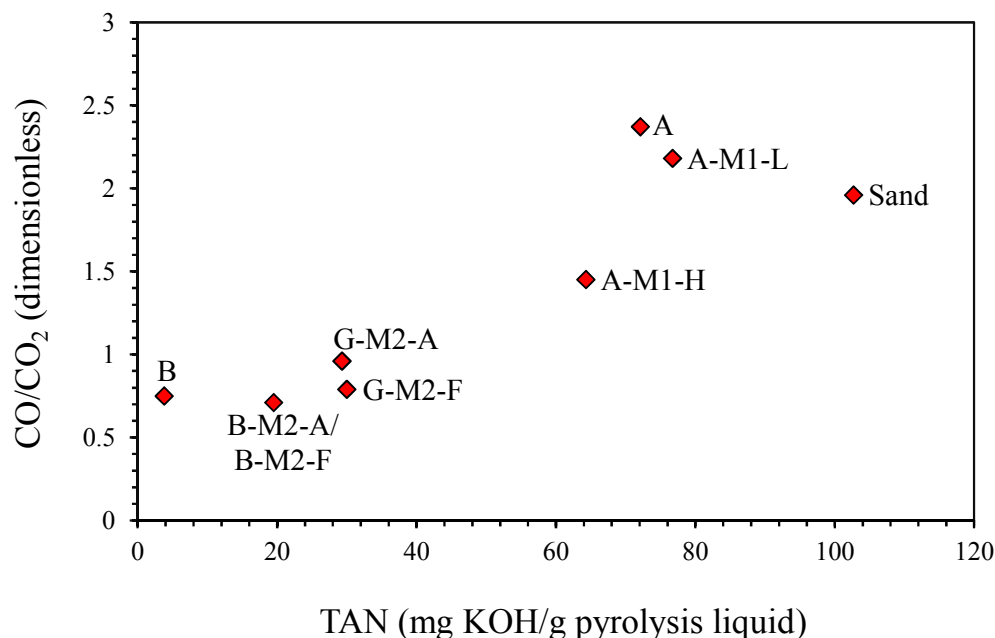


Fig. 4.6. Fast pyrolysis of pine wood over various catalysts performed at 500 °C. Dimensionless CO/CO₂ ratios of the non-condensable gases plotted versus the TAN values of the organic fractions of the condensed liquids. ‘Sand’ refers to the result of non-catalytic experiments.

4.3.1.5 Liquid composition

In the liquid samples produced with the various catalysts in the mini-plant, eighty components were detected via GC×GC-TOF-MS analysis and quantified by GC×GC/MS-FID. For the quantification procedure, the reader is referred to the paper of Djokic *et al.* [180]. The yields of these compounds were calculated in *wt. %* on feed basis (a.r.) and grouped based on their chemical functionalities *viz.*, sugars, aldehydes, acids, furans, ketones, phenols, aromatics (mono-, di-, naphtheno-) and others (unclassified compounds). The individual weight percentages of identified compounds, unidentified compounds, and water in total liquid product were included as well. The results are shown in Table 4.2.

In CFP with acidic zeolites, the catalyst is expected to crack the macromolecules into smaller ones such as anhydrosugars to furans, phenols to mono-aromatic hydrocarbons, furans to hydrocarbons, *etc.* via acid catalyzed dehydration, decarbonylation and decarboxylation reactions [50]. In case of the tests performed with Group 1 type catalysts, the distribution of bio-oil constituents was altered and compared to non-catalytic (sand) experiments. Remarkable decreases in sugars, aldehydes, acids, furans, ketones and others (unclassified oxygenates) were observed (Table 4.2). The decrease in sugars is a pretty well-known effect in catalytic pyrolysis of lignocellulosic biomass with acidic zeolites [100]. In particular, catalyst A eliminated most of the sugars and all the aldehydes while it favoured the production of phenols and aromatics. The presence of the redox metal in catalysts A-M1-H and A-M1-L, and the slight difference in their acidity (ZSM-5 content) compared to that of catalyst A, remarkably changed the product speciation; aromatics and phenols were reduced significantly. Moreover, the fraction of unidentified compounds is much larger for the redox metal containing catalysts if compared to that of catalyst A. Especially A-M1-L catalyst seem to be difficult to characterize on GC×GC-MS. As another observation, none of the catalysts tested in this work yielded any aldehydes – suggesting that aldehydes are the most reactive group in pyrolysis vapours and thus the ones first to be removed in CFP.

For Group 2 and Group 3 catalysts, the compounds that can be quantified by means of GC×GC/MS-FID are very limited. The total weight percentages of identified compounds in pyrolysis liquids vary between 3.1% and 6.3% which does not allow any solid conclusions to be made. This might be due to the size of the molecules which are likely too high for the detection in GC×GC/MS-FID, or because of the ineffectiveness of these catalysts in cracking. Particularly, basic catalysts (Group 2) are known to promote aldol condensation. This carbon-carbon coupling reactions yield longer chain molecules. For that reason, it could well be that some of these heavier resulting molecules can simply not be detected by GC×GC-TOF-MS due their low volatility.

Table 4.2. Fast pyrolysis of pine wood over various catalysts performed at 500 °C. Yields of compounds in the organic fraction of the condensed liquids, classified according to their functionalities, as quantified by GC×GC/MS-FID. The results of non-catalytic (sand) experiments are included for comparison.

	<i>GROUP 1</i>				<i>GROUP 2</i>		<i>GROUP 3</i>		
	Sand	A	A–M1–H	A–M1–L	B	B–M2–A	B–M2–F	G–M2–A	G–M2–F
Identified (total) [wt.% on feed]	19.1	12.6	4.1	7.2	2.5	3.4	2.5	1.7	2.9
(% in total liquid)	(33.3)	(25.1)	(7.5)	(11.7)	(3.9)	(6.3)	(4.8)	(3.1)	(5.8)
Sugars (3 compounds)	2.21	0.06	0.55	1.57	0.29	0.16	0.26	0.11	0.17
Aldehydes (1 compound)	2.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acids (4 compounds)	5.47	1.25	1.11	1.50	0.37	1.45	0.41	0.64	0.85
Furans (9 compounds)	0.78	0.42	0.13	0.14	0.19	0.06	0.06	0.06	0.12
Ketones (8 compounds)	1.01	0.69	0.30	0.58	0.30	0.35	0.34	0.13	0.37
Phenols (18 compounds)	4.37	5.23	1.24	2.25	0.77	1.02	1.03	0.60	1.02
Aromatics (19 compounds)	0.09	4.23	0.22	0.16	0.25	0.11	0.12	0.12	0.17
Others (18 compounds)	2.96	0.74	0.58	0.97	0.31	0.27	0.28	0.05	0.23
Unidentified [wt.% on feed]	17.8	3.7	11.6	27.8	19.5	23.6	21.6	26.6	21.0
(% in total liquid)	(31.0)	(7.3)	(20.9)	(45.5)	(30.5)	(43.7)	(41.4)	(47.7)	(41.4)
Water [†] [wt.% on feed]	20.5	34.0	39.7	26.1	42.0	26.9	28.1	27.5	26.8
(% in total liquid)	(35.7)	(67.6)	(71.7)	(42.7)	(65.6)	(49.9)	(53.8)	(49.3)	(52.9)
Total liquid yield [wt.% on feed]	57.4	50.3	55.4	61.1	64.0	53.9	52.2	55.8	50.7

[†]Results of Karl-Fischer analyses.

4.3.2 In situ catalytic fast pyrolysis – Py-GC/MS results

Py-GC/MS is a rapid and reliable analytical pyrolysis method that can provide the first hints on the way to find the right catalysts before starting any time-consuming larger scale CFP experiments. It allows real time analysis and helps in understanding the chemical mechanisms/pathways leading to pyrolysis liquids with desired properties for certain catalyst/biomass combinations and experimental conditions. Py-GC/MS is a powerful tool for fast pyrolysis studies also because the short residence time of pyrolysis vapours in the micro-pyrolyzer limits the extent of secondary vapour-phase reactions. On the other hand, contact times of these vapours with the catalyst are likely much shorter than in a real pyrolysis setup; this may cause an insufficient conversion of primary pyrolysis vapours to the reformed products in the vapour phase.

Py-GC/MS experiments do not allow any liquid product collection, and thus the exact bio-oil yield cannot be determined. Nevertheless, an estimation of the changes in the yields of total organic volatile compounds can be made through the total chromatographic response areas (TIC) relative to the amount of feed (response area/mg biomass). In this work, detected compounds were classified into twelve groups, with the purpose of clearly showing the compositional changes, and the results are shown in Figures 4.7, 4.8 and 4.9.

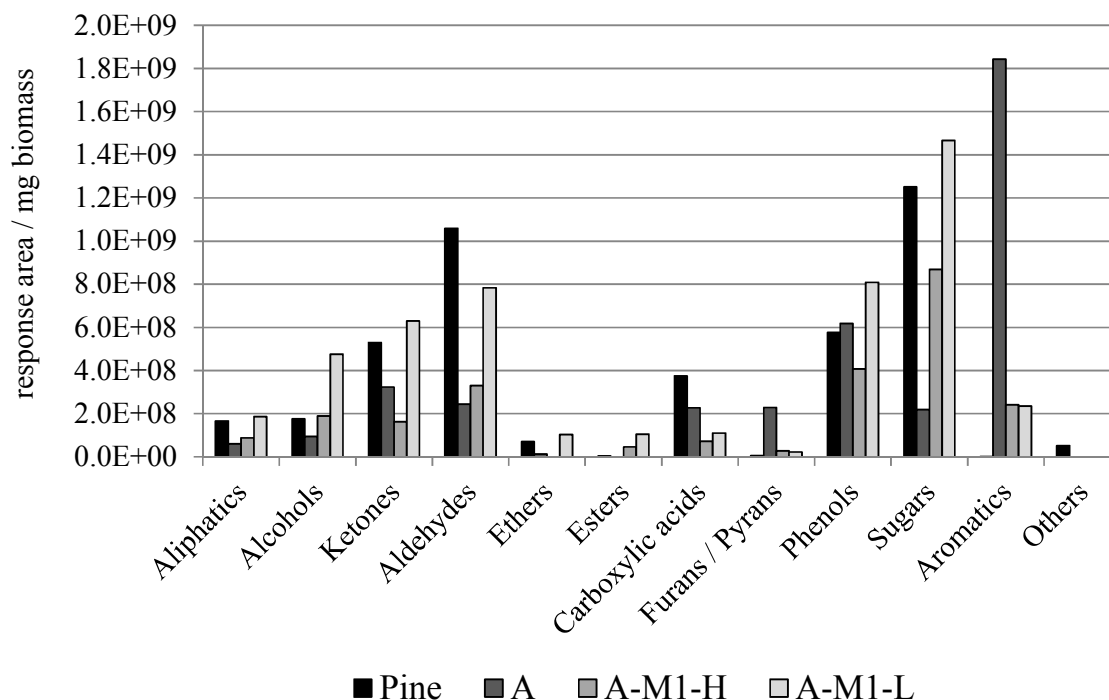


Fig. 4.7. Analysis of pyrolysis vapours of pine wood mixed with Group 1 type catalysts (in response area/mg pine) at 500°C. Functional groups quantified according to their cumulative TIC peak area in py-GC/MS.

Similar to that of GC×GC/MS analyses of CFP-oil, catalyst A decreased the amount of ketones and sugars compared to that of non-catalytic (denoted as pine in the case of py-GC/MS) experiments. Unlike the mini-plant results shown in Table 4.2, aldehydes were observed in py-GC/MS experiments. Aldehydes are among the most unstable compounds in bio-oils. In py-GCMS, both contact time of vapours with the catalysts and the residence times of the reformed vapours are very low, so that the vapours are near instantaneously analysed without being subjected to vapour condensation and storage conditions. However, in larger scale bio-oil production experiments, there is some time between oil production and analysis and thus the unstable aldehydes might already have reacted away (at least partial) during the vapour condensation and/or storage.

In line with the findings in Table 4.2, catalyst A boosted the production of phenols and aromatics in py-GC/MS. This can be attributed to the presence of ZSM-5 in this catalyst which favours the production of aromatics [85]. The increase in the aliphatic hydrocarbons (Fig. 4.7) in case of the redox metal containing catalysts (A-M1-H and A-M1-L) was in line with the literature which suggested that the impregnation of metals to ZSM-5 type catalysts were shown to be effective in producing high yields of hydrocarbons [59]. Unlike the findings shown in Table 4.2, it was seen that in py-GC/MS the vapour phase compound detection with A-M1-L is greater than that of A-M1-H, *viz.* by the larger total response surface area (see also Fig. 4.11). In case of A-M1-L, the bars in Fig. 4.7 are higher for most of the functional groups. The trends in acids, as seen in Fig. 4.7, are also in line with the findings shown in Table 4.2. The presence of redox metal was found to decrease the production of aromatics [173]. In line with this information, the concentrations of aromatics reduced in the presence of A-M1-H and A-M1-L.

In case of the Group 2 type of basic catalysts, py-GC/MS results showed remarkable differences between catalyst B and its metal doped counterparts (B-M2-A and B-M2-F). Catalyst B produced the highest yield of ketones in py-GC/MS among all catalysts studied in this study. In basic catalysts, ketonization is an important mechanism of decarboxylation [194] (basically ketonization is a reaction in which two carboxylic acid molecules form a single symmetric ketone, while H₂O and CO₂ are removed). The higher prevalence of ketones in the presence of catalyst B supports this theory. Another important highlight was that the B-M2 catalysts did not produce any aliphatic hydrocarbons (Fig. 4.9). This can be explained by the absence of acid functionalities in these catalysts to enhance dehydration of organic molecules. With both catalysts tested in py-GC/MS the amount of sugars remarkably decreased, B-M2-A was the most efficient catalyst in the conversion of sugars. Moreover, both basic catalysts showed their poor performance in producing (GC-detectable) aromatics.

Liquid analyses in GC×GC/MS-FID (see Table 4.2) revealed that the presence of metal M2 in B-M2 type catalysts favoured the production of phenols, reduced furans and aromatics in CFP-oil. However, when py-GC/MS results are considered, the high yields of ketones and carboxylic acids found with catalyst B are inconsistent with the results shown in Table 4.2. These inconsistencies could be caused by shorter vapour residence times and the absence of vapour condensation in py-GC/MS which is occurring in the larger real fast pyrolysis process. In general, the yields of these two functional groups in B-M2 catalysed pyrolysis in py-GC/MS are lower than those catalysed by type B. Lower yields, as seen by the lower TIC

(Total Ion Chromatogram) peak area in py-GC/MS as well as the lower concentration reported by GCxGC/MS-FID in the pyrolysis oil revealed that B-M2 type catalysts favour the conversion of vapours to coke and/or heavy molecular weight products at the expense of GC/MS detectables. Basic catalysts may promote aldol condensation reactions, *viz.* two lower molecular weight organic compounds recombine into a heavier (and potential GC undetectable) compound.

One of the most important parameters to determine the performance of a catalyst in CFP is its ability to deoxygenate. As stated before, CO₂ production can be considered as one of the indications (the others are CO and H₂O) of the deoxygenation capability of a catalyst in CFP. Fig. 4.10 shows the response areas of CO₂/mg pine wood identified by py-GC/MS in the pyrolysis vapours with various types of catalysts. Similar to the trends in CO₂ yields shown in Fig. 4.3, basic mixed-metal oxide and γ -alumina catalysts boosted the CO₂ production compared to that of acidic catalysts. These results show that py-GC/MS could be indicative in terms of CO₂ yields. However, py-GC/MS used in this study is not a suitable tool that reveals any data regarding CO and H₂O production, and thus complete deoxygenation capability of a catalyst cannot be determined. If one wants to assess the full deoxygenation capabilities of a given catalyst in analytical pyrolysis, then additional detectors (such as an array of molecular sieves with TCD detectors) need to be installed to quantify the permanent gases – which were outside of the capabilities of the instrument used in this study.

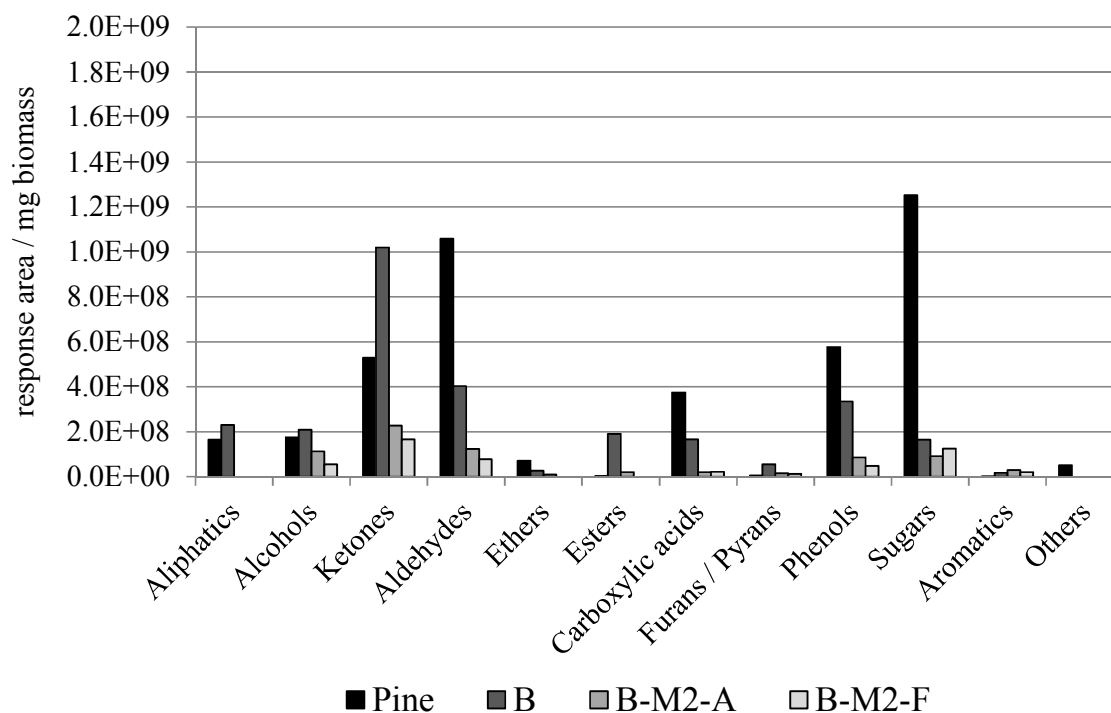


Fig. 4.8. Analysis of pyrolysis vapours of pine wood mixed with Group 2 type catalysts (in response area/mg pine) at 500°C. Functional groups quantified according to their cumulative TIC peak area in py-GC/MS.

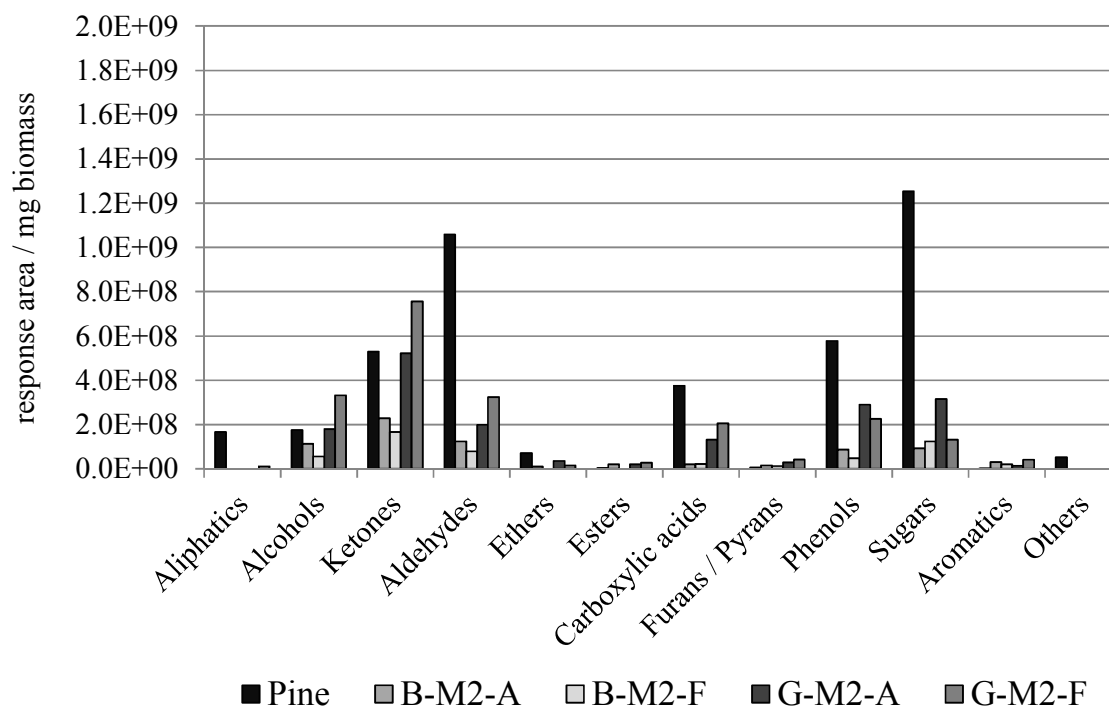


Fig. 4.9. Analysis of pyrolysis vapours of pine wood mixed with Group 3 type catalysts (in response area/mg pine) at 500°C. Functional groups quantified according to their cumulative TIC peak area in py-GC/MS.

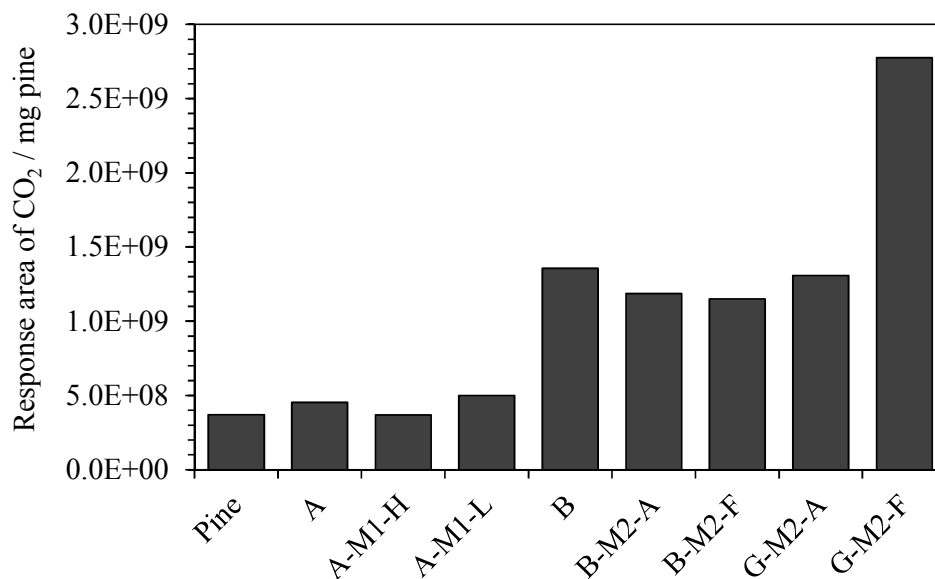


Fig. 4.10. CO₂ quantified by TIC peak area in py-GC/MS in the pyrolysis vapours of pine wood mixed with various types of catalysts, at 500°C.

Primary fast pyrolysis vapours of biomass are composed of non-volatile oligomers and volatile organic compounds. The catalysts promote the cracking of the oligomeric volatile organics into monomeric ones; this increases the amount of (GC/MS detectable) volatiles. On the other hand, the presence of catalysts influences the yields of volatile organic products by causing the cracking of the products to permanent gases, polymerizing them to form cokes, or oligomerizing them into heavier compounds with high boiling points up to a point that they are no longer detectable by GC; all of these reduce the amount of volatiles [144]. Fig. 4.11 shows the total response areas of identified compounds obtained in py-GC/MS tests with the use of various types of catalysts in the pyrolysis of pine wood. When a lower concentration of redox metal added to an acidic zeolite (A-M1-L) the range of detectable compounds with the catalyst increased compared to its parent one. However, the addition of the same redox metal to the same zeolite in higher quantities (A-M1-H) dramatically decreased the range of detectable compounds with the catalyst. Similarly, the addition of metal M2 to the basic catalyst (B-M2-A and B-M2-F) remarkably decreased the range of detectable compounds. However, the addition of the same metal to the γ -alumina catalyst (G-M2-A and G-M2-F) did not show the same effect; response areas were bigger than that of the basic catalysts. This revealed that the same metal on different type of catalysts react differently in CFP experiments performed in py-GC/MS. The identified fraction of the liquid products obtained by GC \times GC/MS (as reported in Table 4.2) are also included for comparison as a secondary axis in Fig. 4.11. These results show that with all catalysts except B-M2-A and B-M2-F, the amount of identified compounds in condensed liquid phase detected by GC \times GC/MS are lower than that of identified vapour phase compounds in py-GC/MS. This might because of some heavier compounds whose boiling points are above that can be readily detected by GC/MS are being formed with these catalysts during vapour condensation.

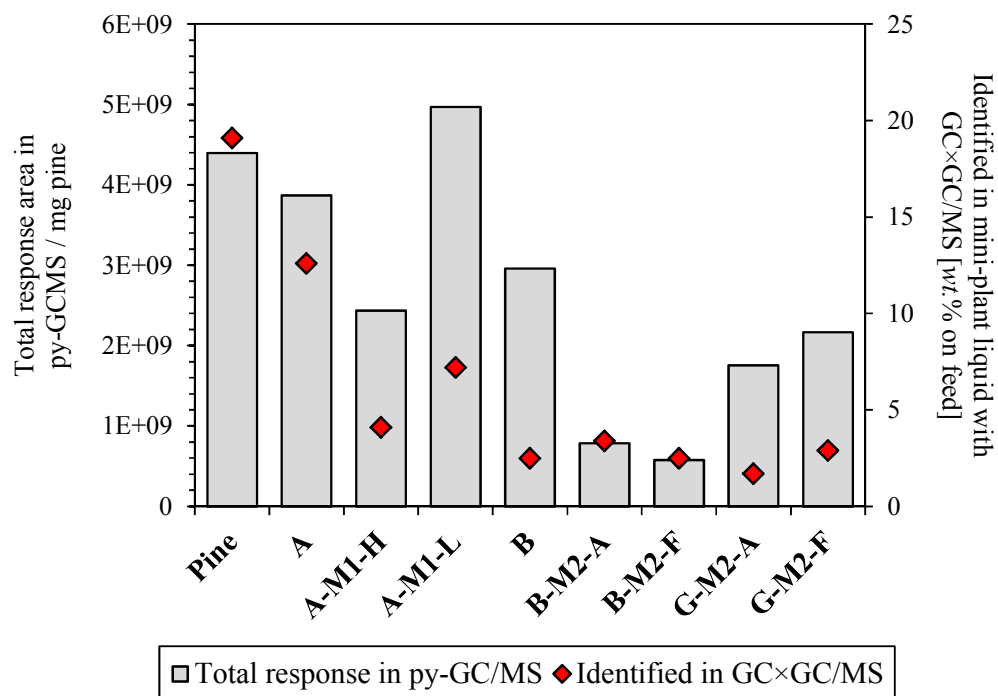


Fig. 4.11. Cumulative response, taken as the total TIC peak surface area in the chromatogram excluding the CO₂ peak, obtained from py-GC/MS tests with the use of various types of catalysts in the pyrolysis of pine wood (in response area/mg pine) at 500°C. Unidentified fraction of organic compounds in GC×GC/MS (in wt.% on feed basis) are included for comparison.

In conclusion, the low percentage of quantifiable organics in the pyrolysis oil, as well as in the pyrolysis vapours in case of analytical pyrolysis (Table 4.2 and Figures 4.7, 4.8, and 4.9) are due to the limitations of the GC×GC–MS and py-GC/MS analysis. Additional problems in quantifying bio-oil or the constituents in pyrolysis vapours by means of GC–MS is that certain pyrolysis compounds are poorly defined in existing MS libraries and sometimes calibration standards are not existing. Unless the py-GC/MS is not quantitatively calibrated for a number of well-defined specific compounds of interest, it is only partially indicative for the performance of a catalyst in CFP. Moreover, analytical pyrolysis systems (*i.e.* py-GC) employ very short vapour residence times and do not include the phenomena such as vapour condensation. Consequently, the chemistry associated with longer vapour trajectories and vapour condensation, which do occur in larger scale pyrolysis setups, will not be captured. All these limitations inherent to the instrumental technique of gas chromatography should be kept in mind when assessing performances of catalysts in catalytic pyrolysis based on oil or vapour composition. For the exact determination of the deoxygenation performance as well as to assess the complete composition and quality of the bio-oil, larger scale catalytic experiments are indispensable.

4.4 Conclusions

The main target of catalytic fast pyrolysis of lignocellulosic biomass is to deoxygenate the liquid product as much as possible while minimizing the coke formation on the catalyst. Complete deoxygenation however, would result in producing only hydrocarbons (or just carbon in the worst case) at a very low yield. Hence, catalysis should be applied rather to steer the oxygen functionalities in the pyrolysis vapours, resulting in the production of certain fuel compounds or chemicals (aromatics, phenols, alcohols, furans, *etc.*) in the produced liquid. It should be noticed here that the selection of a catalyst for catalytic fast pyrolysis of biomass is determined in the first place by the requirements imposed by any future user of the liquid product. As an example, the further (co-) processing in a refinery FCC unit would at least require a significant degree of deoxygenation and a good miscibility with the fossil feedstock. This work was meant to assess the efficiency of various catalysts in terms of their capability to deoxygenate the pyrolysis vapours, and observe their potential to produce a liquid mixture that could be used as a renewable feedstock in petrochemical industries.

In this work, eight proprietary catalysts were tested. They were divided into three groups based on their acidity, the type of carrier, the type of active metal added, and also according to being aged or fresh. Included are a ZSM-5 containing acidic zeolite (A) and its redox metal added but lower ZSM-5 containing counterparts (A-M1-H and A-M1-L), a basic mixed-metal oxide catalyst (B) and its metal added aged (B-M2-A) and freshly calcined (B-M2-F) counterparts, and freshly calcined (G-M2-F) and aged (G-M2-A) versions of a basic metal modified γ -alumina catalyst. The term ‘aging’ represents the anticipated adsorption of water and/or CO₂ on the catalyst from its contact with air.

In the continuously operated mini-plant experiments, the presence of catalysts led to the production of coke, non-condensable gases and additional water at the expense of organics and char. However, the quality of the obtained liquid products was altered in various ways, depending on the catalyst type and its active metal content. Different mechanisms of oxygen removal (decarbonylation, decarboxylation, and dehydration) were observed. In the case of metal added catalysts, effect of the metals on the water gas shift reaction, pushing it in the direction of CO₂ and H₂ production, may be well possible.

The adjustment of the redox metal (metal M1) content in a catalyst was seen to significantly change the vapour phase reaction chemistry and thus the product distribution. The acidic zeolite catalyst with a low loading of redox metal (A-M1-L) gave a higher yield of liquid organics than its higher-concentration redox metal containing counterpart (A-M1-H). Moreover, a higher redox metal content was shown to promote water and CO_x production. The lower CO/CO₂ ratio found with A-M1-H catalyst revealed that a higher redox metal content favours the decarboxylation (oxygen removal via CO₂ production). As another observation, the presence of redox metal contributed notably to the suppression of coke production.

The higher water yield observed in the presence of basic catalyst (catalyst B, metal-free parent catalyst) revealed that dehydration (oxygen removal via H_2O production) is the main deoxygenation mechanism for this catalyst. The addition of metal M2 to this catalyst resulted in a decrease in water production, while boosting the production of non-condensable gases and in particular the CO, CO_2 , and H_2 yields. A slightly lower CO/ CO_2 ratio revealed that the presence of metal M2 in the basic catalyst is capable of changing the mechanism of oxygen removal compared to that of its parent one; it favoured the decarboxylation mechanism more than dehydration or decarbonylation mechanisms.

Concerning the difference between fresh and aged catalysts the general observation is that the freshly calcined catalysts show more activity in a sense of a notably increased conversion of organics to the undesired products coke, non-condensable gases (mainly CO_x) and water. The lower activity observed with the aged catalysts might be due to the adsorption of water and/or CO_2 on these catalysts during their long-term storage. This may cause the blockage of the pores and shielding of active sites.

In order to determine the performances of the catalysts tested under identical process conditions, two separate evaluations are made based on various defined criteria. The considered criteria are the deoxygenation by CO_2 (the preferred route for deoxygenation), the yield of organic liquid phase, H/C ratio of the organic liquid phase, O/C ratio of the organic liquid phase, coke yield, the production of desirable compounds, energy content in the organic liquid phase, and the percentage of the detectable components in the organics. Although subjective, and depending on any target applications, the order of the weight factors is determined based either on the deoxygenation requirements (Table A.4.3a in the Supporting Information) or on the production of desirable compounds in high yields (Table A.4.3b in the Supporting Information).

The evaluation based on the deoxygenation requirements reveals that the best performing catalyst was the metal added freshly calcined basic mixed-metal oxide catalyst (B-M2-F), while the poorest performance was shown by the ZSM-5 containing acidic zeolite (A). Acidic catalyst with a low concentration of metal (A-M1-L), and freshly calcined basic metal-modified γ -alumina catalyst (G-M2-F) showed similar performances to that of B-M2-F. On the other hand, when the target is the production of desirable compounds in high yields, A-M1-L performed as the best catalyst. B-M2-F and G-M2-F showed quite similar performances to that of A-M1-L. The basic mixed-metal oxide catalyst (B) showed the poorest performance in this evaluation. The difference in catalyst performances is obvious with respect to the metal loading and the amount of it. In general, metal doped catalysts performed better than their parent counterparts. Moreover, in both evaluations, freshly calcined catalysts performed better than their aged counterparts.

Concerning the micropyrolysis tests, it can be concluded that, unless the py-GC/MS is not quantitatively calibrated for a number of well-defined specific compounds of interest, it is only partially indicative for the performance of a catalyst in CFP. Furthermore, micropyrolysis systems are limited by the type of separation and detector used (*e.g.* GC/MS) with respect to the kind of pyrolysis compounds being quantified. It can therefore be concluded that optimal micropyrolysis configurations (dedicated columns and detectors that,

for instance, also allow dedicated quantification of permanent gases) could give indicative results for catalyst performance. As such, an optimally configured py-GC/MS can be used as a rapid screening tool prior to the time consuming larger scale CFP experiments. For the exact determination of the deoxygenation performance as well as to assess the complete composition and quality of the bio-oil, larger scale catalytic experiments are indispensable.

Overall, as it describes the results obtained with the use of various catalysts, this chapter provides a good example of the tuning in both product properties and reaction pathways that can be achieved with a catalyst in CFP.

Chapter 5

Effect of successive catalyst regeneration in catalytic pyrolysis of pine wood

Abstract

The main product of biomass fast pyrolysis is a liquid mixture of numerous organic molecules with water that is usually called pyrolysis oil or bio-oil. The research discussed in this chapter was meant (1) to validate a new, continuously operated pyrolysis set-up and (2) to investigate the effect of a repeatedly regenerated ZSM-5-based catalyst (eight reaction/regeneration cycles in total) on the yields and compositions of the pyrolysis products in relation to the applied process conditions and on the catalyst itself. The reliability of the set-up has been proven by multiple repetitions of non-catalytic and catalytic (in situ) pyrolysis experiments for pine wood at 500 °C under identical conditions. As a result, the mass balance closures for all experiments varied from 92 to 99 wt.%, while the scatter in measured data was always less than 5%. Changes in the performance of the repeatedly regenerated catalyst have been observed via detailed analysis of the bio-oil (GC×GC-FID and GC×GC-TOF-MS, Karl-Fischer), the non-condensable gases (micro-GC), and the carbonaceous solids (elemental analyser, BET surface area). Along the reaction/regeneration sequence, the yield of organics increased, while water, carbonaceous solids, and non-condensable gases decreased. Trends in pyrolysis product yields converging to that of non-catalytic levels were observed, which revealed that the influence of the catalyst slowly declined. The main observation was that the catalyst partially loses its activity in terms of the product distribution along the reaction/regeneration sequence, while retaining sufficient activity in producing the target chemical compounds.

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5.1 Introduction

Increasing prices, shortage, storage, safety, and transport of the fossil fuel feedstocks have led to an increasing interest in the use of renewable lignocellulosic biomass resources. Fast pyrolysis, the rapid thermal decomposition of matter in the absence of oxygen followed by direct condensation of vapours, is an emerging and cost-effective thermo-chemical method to convert lignocellulosic biomass into a high quantity of a liquid [197] (*i.e.* pyrolysis liquid, bio-oil). However, before pyrolysis liquids can be used in replacing petroleum fuels or as a source for chemicals, their quality needs to be improved. The use of heterogeneous catalysts in the fast pyrolysis process itself (*i.e.* catalytic fast pyrolysis; CFP) can induce reactions that cause a change in oxygen functionalities, increase the calorific value, and improve the stability of the bio-oil. This way, the liquid product (*i.e.* CFP-oil) can be deoxygenated to a greater extent and become more similar in chemical composition to current gasoline and diesel fuels than the conventional crude bio-oil [41,42].

One of the problems in CFP of biomass, hardly discussed in the literature, is the rate and extent of deactivation of the catalyst. Deactivation implies the physical, chemical, thermal, and mechanical degradation of the catalyst leading to a reduced activity and selectivity [198,199]. Various mechanisms causing catalyst deactivation are known, such as (1) fouling, the physical adsorption of certain species on the catalyst surface that causes blocking of pores and active sites; (2) poisoning, the change of the surface structure due to the chemisorption of species on active sites; (3) attrition, which is the loss of catalytic material due to physical erosion, and (4) dealumination of the zeolite Si/Al framework by hydrolysis in the presence of acids and steam [126,198]. In catalytic pyrolysis of biomass, deactivation can be mainly attributed to coke deposition, which blocks the pores and poisons the active sites of zeolites [200–202]. Some degree of deactivation by deposition of contaminants (ash) originally present in the biomass cannot be excluded either [29].

Similar to conventional FCC processes, the deactivated catalyst can be regenerated by a high temperature oxidative treatment meant to burn the coke off the catalyst and thereby restore its activity [126,202]. In the case of a biomass, however, the associated coke contains more oxygen and hydrogen than coke from fossil fuels. Regeneration of the catalysts thus yields water and CO_x, which for ZSM-5 and similar structured catalysts, leads to dealumination and loss of active (acid) sites [104,132,203]. A possible solution to this problem is a two-step regeneration method [126,203]. In a first low-temperature step (*ca.* 250 °C) most of the water will be released, while in a second step the temperature can be raised (to 400–700 °C) to burn the coke [125,132]. In this way the catalyst degradation may be limited because of the reduced exposure to an atmosphere containing steam at high temperatures.

A number of studies have addressed the topic of catalyst regeneration after their use in catalytic pyrolysis of biomass. A few of these studies deal with *multiple* regenerations and reuse in pyrolysis (see Table A.5.1 in the Supporting Information). Williams *et al.* [195] studied the deactivation and regeneration of ZSM-5 in the upgrading of wood pyrolysis vapours in a fluidized bed reactor (7.5 cm diameter \times 100 cm high). They regenerated the catalyst in a furnace at 550 °C in the presence of air for 8 h and found that the regeneration decreases the catalytic activity. With the increasing number of reaction/regeneration cycles (in total five cycles were performed), less alkene gases were produced, oxygen containing compounds were converted less efficiently, and the carbon content of the final oil was reduced by the production of additional coke. In addition, regeneration caused a less efficient conversion of hydrocarbons to aromatics, which were the products of interest. After five reaction/regeneration cycles the production of monocyclic aromatics was reduced with 50 wt.% compared to the use of the fresh catalyst. More recently, Aho *et al.* performed catalytic pyrolysis of pine wood in a 102 mm long dual-fluidized bed reactor (*ex situ*) [132] and a 590 mm long fluidized bed reactor made of Pyrex glass (*in situ*) [104,125]. The zeolite catalysts were regenerated (single reaction/regeneration cycle in each studies) batchwise in an oven while two stages of constant temperature (250 and 450 °C) were applied. It was concluded that some Brønsted acid sites were lost during regeneration but the surface area of the catalyst regained. Carlson *et al.* [92] and Paasikallio *et al.* [86] studied the stability of the catalyst during CFP. After purging their fluidised bed with N₂ to ensure pyrolytic conditions for the experiment, they replaced the N₂ with air for single-step catalyst regeneration. In the work carried out by Carlson *et al.*, deposited metal impurities were detected on the catalyst; however, the acid sites on the zeolite were not affected after 10 reaction/regeneration cycles. Paasikallio *et al.* found that a catalyst regeneration temperature of approximately 600 °C was not high enough to remove all of the coke deposits. Increasing the temperature to about 680 °C increased the effectiveness of the coke combustion but resulted in a lower post-regeneration specific surface area for the catalyst.

In this work, the catalytic fast pyrolysis of small pine wood particles has been studied by experiments in a newly designed mechanically agitated bed reactor at 500 °C containing ZSM-5-based catalyst particles mixed with sand in a weight ratio of 1:14. The intention was to examine the effect of repeated catalyst regeneration on the product yields and composition, as well as on the properties of the catalyst itself (coke deposition and BET surface area). Eight cycles of catalytic pyrolysis and subsequent catalyst regeneration were carried out in total. The performance of the catalyst was tested under realistic (harsh) conditions, such as

- (1) Mechanical mixing of the catalyst/sand bed during the pyrolysis runs, which may promote attrition and crushing of the catalyst particles;
- (2) Higher catalyst regeneration temperatures of up to 600 °C;
- (3) Regeneration in the presence of the pyrolysis char, leading to the accumulation of biomass ash in the reactor bed material over the successive reaction/regeneration cycles.

5.2 Experimental section

5.2.1 Materials

Pine, obtained from Bemap Houtmeel B.V., Bemmelen, The Netherlands, was used as biomass feedstock in all experiments. This feedstock was sieved to obtain a fraction with particle sizes between 1 and 2 mm. The moisture and ash content were determined to be 7.52 wt.% and 0.33 wt.% on a “as-received” basis (a.r.), respectively. The proximate analysis data, the elemental composition and the higher heating values (in as-received and dry basis) of the pine wood are listed in Table 5.1.

Silica sand (obtained from PTB-Compaktuna, Gent, Belgium) with a mean diameter of 250 μm and a particle density of 2650 kg/m³ (compacted bulk density = 1660 kg/m³) was used as bed material for non-catalytic experiments and blended with the catalyst in the case of the in situ catalytic experiments.

A commercial, spray-dried heterogeneous ZSM-5-based catalyst, indicated as ‘Type A’, was prepared and supplied by Albemarle Catalyst Company B.V. (Amsterdam, The Netherlands). Physical and chemical properties of this catalyst can be found in Appendix A (this appendix is confidential and can only be accessed by signing a confidentiality agreement). Prior to the delivery, this catalyst was calcined in air at 500 °C for 1 h to decrease the moisture content of the catalyst to below 1 wt.%.

Table 5.1. Properties of pine wood.

Proximate analysis (wt.%)	
Fixed carbon (d.b.)	14.96
Volatiles (d.b.) [ASTM E872-82]	84.76
Moisture (a.r.) [ASTM E871-82]	7.52
Ash (d.b.) [ASTM E1755-01]	0.33
Ultimate analysis (d.b.) [wt.%]	
C	47.10
H	5.90
O	46.40
N	0.04
S	0.06
Alkali metals (d.b.) [mg/kg]	
K	346.2
Na	10.1
Mg	112.8
Ca	767.0
HHV (a.r.) [MJ/kg] ^a	18.29
HHV (d.b.) [MJ/kg]	19.77

^a Calculated by using the Milne formula [204].

5.2.2 Experimental unit

Non-catalytic and in situ catalytic pyrolysis experiments have been carried out in a fully controlled, continuously operated lab-scale set-up that enabled the production of bio-oil samples (*ca.* 50 g/run) suitable for a full physicochemical characterization. A scheme of the unit is shown in Fig. 5.1.

The electrically heated pyrolysis reactor vessel is built from stainless steel and has a design similar to the usual bubbling fluidized reactors. Its bed height, inner bed diameter, freeboard height, and freeboard diameter are 45, 7, 35, and 10 cm, respectively. A specially designed mixer was placed inside the reactor to ensure uniform mixing of the content of the bed. Cold model mixing and bed material discharging tests, performed prior to the experimental work, visually revealed the well-mixing of the bed contents (catalyst and sand) without any segregation. The rotation frequency of the mechanical mixer is adjustable via a rotor, and with the continuous rotation of the shaft, efficient mixing of the bed material is achieved and immediate contact of biomass particles with turbulently moving bed material ensured.

Unlike fluidized bed reactors in which an inert gas is used to mix/fluidize the bed, the purpose of the inert gas in this set-up is to remove the pyrolysis vapours from the reactor. The addition of a mechanical mixer inside the reactor allows the inert gas flow rate to be lower than the minimum fluidization velocity, thereby increasing the contact time of the pyrolysis vapours with the catalyst, while minimizing the entrainment of the catalyst particles out of the reactor and preventing the segregation of partly-converted char particles on top of the bed.

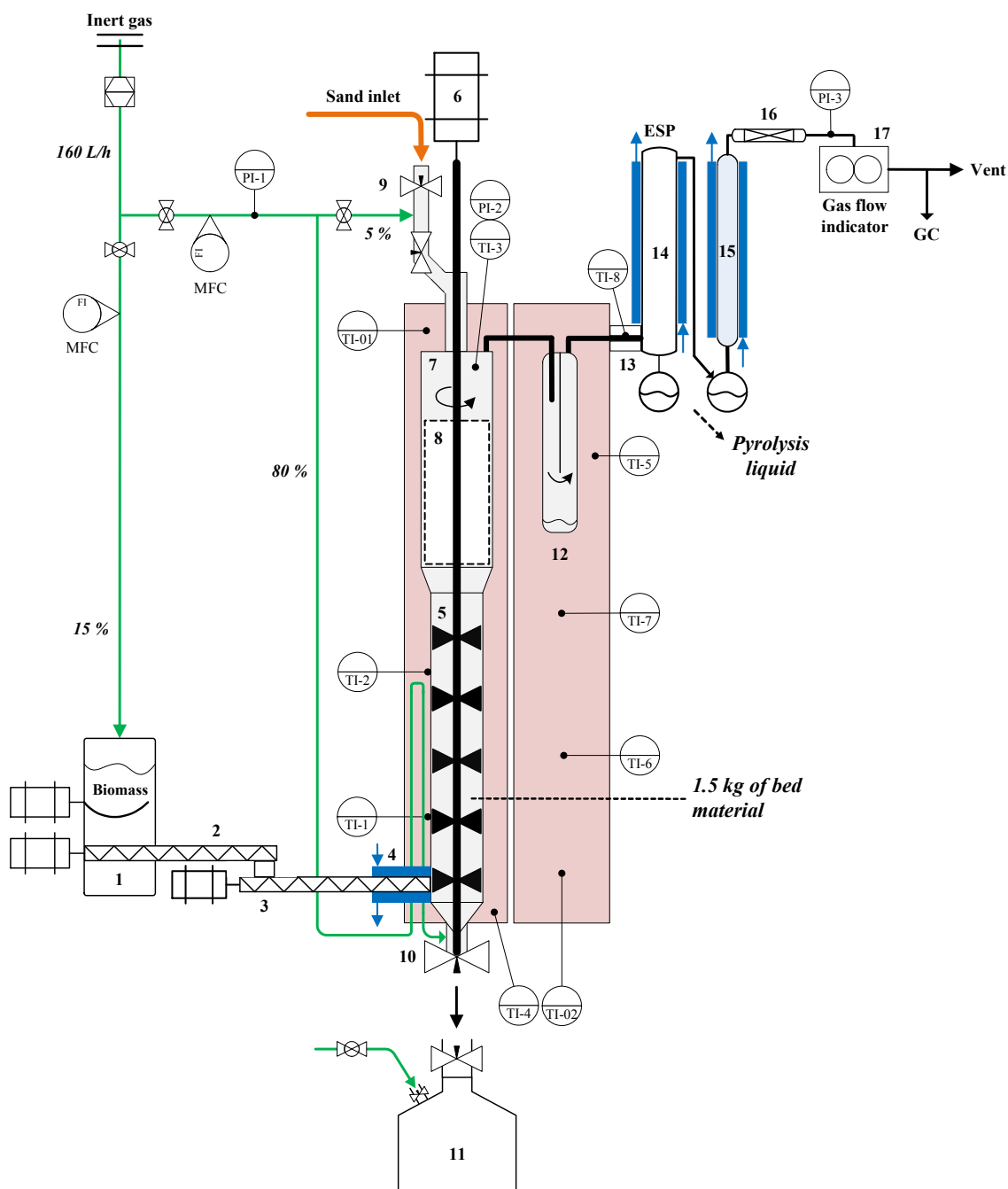


Fig. 5.1. Scheme of the pyrolysis set-up. (1) biomass storage hopper; (2) hopper feeding screw; (3) biomass feeding screw; (4) cooling jacket; (5) mechanical mixer; (6) mixer rotor; (7) pyrolysis reactor vessel; (8) spacer; (9) valve couple for sand inlet mechanism; (10) reactor vessel bottom valve; (11) solids (sand and char) collection vessel; (12) knock-out vessel; (13) insulated condenser inlet line; (14) water cooled electro-static precipitator; (15) water cooled spiral glass condenser; (16) cotton filter; and (17) gas flow indicator.

5.2.3 Pyrolysis experiments

The pine wood (a.r.) is introduced into the reactor by a twin-screw from a sealed feed hopper. Inert gas (N_2) enters the system at three points, *viz.*, via the feed hopper (~15 %), the plenum chamber (preheated, ~80 %) and the top of the pyrolysis reaction vessel (~5 %). The flow rates of both streams were precisely controlled by individual mass flow controllers. A total inert gas flow rate of *ca.* 160 L h⁻¹ was applied in all experiments. A knock out vessel is placed at the exit of the reactor to remove and collect fine particles. Pyrolysis vapours flow into a tap water cooled liquid recovery system that consists of an electrostatic precipitator (ESP, operated at 15 kV) and a spiral condenser (glass). The non-condensable gases (NCGs) leave the system after passing through a cotton filter and a gas flow measurement. It was decided to keep the experimental run time at 60 min in order to produce sufficient bio-oil for different types of analyses as well as to reach a sufficiently high accuracy for the mass balance determination. Moreover, a relatively long experimental run time allows the biomass particles to be completely devolatilized at the reaction temperature. Approximately 100 g of pine wood is fed during every run, which could be determined by measuring the mass difference between pine in the storage hopper and in the feeding screw, before and after each experiment. For the non-catalytic experiments, 1.5 kg pure sand was used as a reactor bed material, while for the in situ catalytic experiments a catalyst-sand mixture of 1.5 kg (catalyst-to-sand mass ratio of 1:14) was used. The reason for selecting a catalyst-to-sand weight ratio of 1:14 was to maintain the weight hourly space velocity WHSV [h⁻¹] at a value of around 1 (see Table 5.2).

5.2.4 Collection and analysis of pyrolysis products

The products obtained from catalytic pyrolysis are divided into non-condensable gas (NCG), liquid products (organics and water), and carbonaceous material (coke/char).

The average NCG flow rate ($\Phi_{g,avg}$; L/h) was calculated by subtracting the average inert gas flow from the total gas flow. During the run, six gas samples were taken at intervals of 10 min by using a gastight syringe. The composition of non-condensable gases was determined off-line using a micro-GC (Varian 490-GC) equipped with two TCD detectors and two analytical columns. The following gaseous compounds were measured: CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, and H₂. The sum of C₂H₄, C₂H₆, C₃H₆ and C₃H₈ will be further referred to as C₂₊. For detailed information concerning the NCG yield calculations, the reader is directed to our earlier publication [100].

Prior and subsequent to each experiment, the ESP ($m_{ESP,in}$ and $m_{ESP,out}$), the glass condenser ($m_{gc,in}$ and $m_{gc,out}$) and the cotton filter ($m_{cf,in}$ and $m_{cf,out}$) (including their piping) were weighed. The mass difference should be equal to the measured amount of bio-oil produced. In non-catalytic experiments a homogeneous single phase, and in catalytic experiments a two phase liquid (aqueous + heavy fractions) were collected in the ESP. In order to recover the residual bio-oil fractions on the condenser walls, all related parts were rinsed with a known amount of tetrahydrofuran (THF). By using THF, a homogeneous (single-phase) liquid mixture was obtained. This mixture was then filtered over a 10 μ m MN640w filter (Macherey-Nagel, Düren, Germany) and the amount of retained solids (m_{fs})

was excluded from the total amount of bio-oil. In order to prevent the solid losses and ensure a constant catalyst concentration in the bed inventory, these retained solids were included in the gross amount of bed material prior to the regeneration step. The bio-oil yield was calculated using Eq. 5.1:

$$Y_{\text{biooil}} = \left[(m_{\text{ESP,out}} - m_{\text{ESP,in}}) + (m_{\text{gc,out}} - m_{\text{gc,in}}) + (m_{\text{cf,out}} - m_{\text{cf,in}}) - m_{\text{fs}} \right] \cdot \frac{100\%}{m_{\text{feed}}} \quad (\text{Eq. 5.1})$$

The bio-oil + THF mixtures were analysed for the H₂O content (Karl Fischer titration) and their chemical composition (GC×GC/MS-FID). For detailed characterization of bio-oils, a combination of GC×GC–FID and GC×GC–TOF–MS was used to get a high chromatographic resolution and on the other hand maximal agreement between both chromatograms [100,180]. The GC×GC setup consisted of a Thermo Scientific TRACE GC×GC, obtained from Interscience Belgium, and has been discussed previously [181,182]. The first column was a RTX-1 PONA (50 m L × 0.25 mm I.D., 0.5 µm df) and the second column was a BPX-50 (2 m L × 0.15 mm I.D., 0.15 µm df). The oven temperature program started at –40 °C and was ramped up to 300 °C at a heating rate of 3 °C/min [181,182]. For GC×GC, the modulation period was 7 s. The mass fraction of each compound is calculated using the mass fraction of the internal standard, peak volumes obtained using the GC, and the relative (to methane) response factors of the compounds for the FID. The response factors for a large set of typical compounds that are present in bio-oils are determined experimentally from a set of well-defined calibration mixtures [180]. Response factors of compounds that were not included in the calibration mixture, and that are detected in bio-oils, were calculated using the effective carbon number approach [205]. After the identification and quantification of the compounds present in the bio-oils, the compounds were classified into eight different groups, namely sugars, aldehydes, acids, furans, ketones, phenols, aromatics and others, according to their functional groups. More details can be found in Yildiz *et al.* [100] (Chapter 3 in this thesis) and Djokic *et al.* [180]. Every analysis was done in triplicate, and averaged data are reported with the corresponding standard deviations.

Carbonaceous solids (CS) are the sum of char, heterogeneous coke (defined as the coke deposited on the catalyst), and system deposits. System deposits can be defined as the carbonaceous matter other than char in the case of the non-catalytic experiments, and an average value of *ca.* 5 wt.% was obtained after having been checked a number of times. The amount of carbonaceous solids was determined by subjecting the collected solids to L.O.I. analysis which refers to the weight loss of a sample after ignition and combustion in air which is carried out in a muffle furnace (Carbolite AAF 1100) at 600 °C for 6 h. Solids are composed of the contents of the solids collection vessel (char + bed material) and knock-out vessel, and solid filtrate (washed with THF) from bio-oil filtration. The yield of carbonaceous solids was calculated using Eq. 5.2:

$$Y_{\text{cs}} = (m_{\text{solids,i}} - m_{\text{solids,f}}) \cdot \frac{100\%}{m_{\text{feed}}} \quad (\text{Eq. 5.2})$$

The BET surface area of spent and regenerated catalysts was determined by a Gemini V surface area analyser from Micromeritics.

The elemental composition of char samples were determined by a Thermo Scientific Flash 2000 Organic Elemental Analyser. The elemental distribution for the pyrolysis products can be found in Table A.5.2 in the Supporting Information.

The Dulong equation (*Eq. 5.3*) for a semi-quantitatively calculation of the higher heating value's (HHV) of fuels or fuel resources such as coal, biomass, pyrolysis oil, and biodiesel from the elemental weight composition, was used to calculate the HHV's of bio-oil samples, where C, H, and O are carbon, hydrogen, and oxygen in weight percentages, respectively [177]:

$$\text{HHV}(\text{MJ} \cdot \text{kg}^{-1}) = (337\text{C} + 1442(\text{H} - \text{O}/8))/1000 \quad (\text{Eq. 5.3})$$

5.2.5 Successive regeneration of the catalyst

The effect of catalyst regeneration on its activity was investigated by comparing the product yields and the compositions of bio-oil and non-condensable gases. After each experiment, the bed material (char, sand, and the spent catalyst mixture) was removed from the reactor. Small amounts of char and spent catalyst were taken for their compositional analyses, and the rest was subjected to a regeneration procedure in a muffle furnace based on the procedure proposed by Aho *et al.* [125] Here the temperature was increased from ambient to 250 °C with a ramp rate of 4.5 °C min⁻¹, and kept isothermal at 250 °C for 40 min. Then the temperature was raised to 600 °C with a temperature increase of 5 °C min⁻¹, and kept at 600 °C for 5 h. The reason to select this relatively high catalyst regeneration temperature was to maximize the removal of the heterogeneous coke deposited on the catalyst surface. The application of an even higher regeneration temperature was considered undesirable because of the risk of the surface area loss of the catalyst. The temperature was then decreased to 105 °C (instead of ambient temperature) to prevent moisture absorption. Finally the catalyst–sand mixture, regenerated in this way, was stored in the oven at 105 °C until the next experiment. Subsequently, it was fed back to the pyrolysis reactor and the experiment was repeated. In total, eight reaction/regeneration cycles were carried out.

5.3 Results and discussion

5.3.1 Mass balance closure and reproducibility

The reproducibility of the setup was tested by performing a number of non-catalytic and in situ catalytic benchmark experiments under identical process conditions. These operating conditions are listed in Table 5.2.

Table 5.2. Operating conditions non-catalytic and catalytic experiments.

t_{run} [min]	60	
T_{reactor} [°C]	500	
U [m/s] ^c	0.012	
U/U_{mf} [-] ^c	0.22	
$(U/U_{\text{mf}})_{\text{total}}$ ^d	0.35	
	<i>Non-catalytic</i> ^a	<i>Catalytic</i> ^b
Φ_{pine} [g/h]	116.5	111.0
Φ_{N_2} [L/h]	164.6	158.4
$m_{\text{bed material}}$ [kg]	1.5	1.5
Ratio of catalyst/sand in mixture [wt/wt]	-	1:14
$m_{\text{bed material}}/m_{\text{pine}}$ [wt/wt] ^c	12.9	13.5
WHSV [h ⁻¹] ^f	-	0.9
Final char hold-up [vol.%] ^c	12.9	11.3
$\tau_{\text{vapours, in the bed material}}$ [s]	10.2	10.6
$\tau_{\text{vapours, reactor freeboard}}$ [s] ^g	32.8	34.9
$\tau_{\text{vapours, total}}$	43.0	45.5

Explanations:

^a Averages of five non-catalytic experiments (NC) under identical process parameters.

^b Averages of three in situ catalytic experiments (R0) under identical process parameters.

^c On the basis of nitrogen flow only (pyrolysis vapour free stream).

^d On the basis of combined flow rate of nitrogen + pyrolysis vapours (non-catalytic case).

^e After $t_{\text{run}}=60$ min.

^f WHSV (weight hourly space velocity) = mass flow rate of feed [g/h] / mass of catalyst [g].

^g The residence time of hot vapours after they leave the bed, until they reach the condenser inlet.

The total mass balance closures calculated for the experiments varied between 92.1 wt.% and 97.8 wt.% for the non-catalytic and 93.1 wt.% and 99.2 wt.% for the in situ catalytic experiments, respectively. Small but inevitable product losses, which are inherently related to this scale of operation, are the reason that the mass balances could not be closed completely. The average product yields, on an “as-received” feed basis, are reported in Fig. 5.2, and were within the range of what has been previously reported in the literature [77]. In this figure, the error bars represent standard deviations in absolute %’s for all experiments. Variations were mainly due to the handling, collection and weighing of the products. The scatter in the product yields is always less than 5%, indicating reproducibility sufficient for observing trends in all similar experiments.

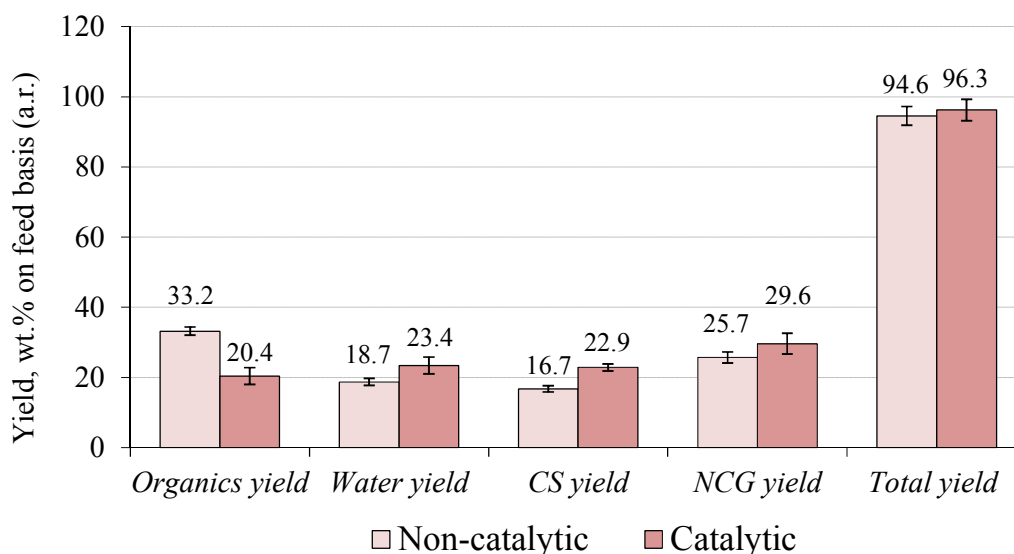


Fig. 5.2. Yields of organics, water, carbonaceous solids (CS), non-condensable gases (NCG), and total yields obtained from five non-catalytic and three in situ catalytic fast pyrolysis with fresh catalyst experiments of pine wood at a T_{reactor} of 500 °C. Standard deviations are represented in absolute %.

5.3.2 Effect of the catalyst and vapour residence time on pyrolysis product yields

To maximize bio-oil production in biomass fast pyrolysis, vapour residence times less than 1 s are considered essential [206]. However, in the present set-up, vapours reside longer in the hot zones due to the specific design of the reactor. Secondary cracking of the primary products may occur to a significant extent which will increase the gas yields, reduce the liquid yield, and affect the bio-oil properties as well [207]. At the same time however, these higher vapour phase residence times could promote the secondary vapour-phase cracking reactions [86]. Even though the composition of the pyrolysis oil may be dependent on the vapour residence time to a certain extent, in order to disclose the quality of our liquid product, we compared the chemical composition of a standard non-catalytic bio-oil from this study’s setup with a reference bio-oil obtained from the continuous fast pyrolysis plant (with 150–200 kg/h of feed intake) of Biomass Technology Group, BTG (Enschede, The Netherlands). These results revealed that, although the produced quantity of our liquid product was lower, the

chemical composition of it is similar to that produced in this continuous fast pyrolysis pilot plant (see Fig. A.5.1 in the Supporting Information).

In the literature, catalytic fast pyrolysis mechanisms are presented, describing the reactions that take place when fast pyrolysis of biomass is carried out in the presence of zeolites [70,92]. Generally, the organic compounds formed in non-catalytic fast pyrolysis undergo an additional conversion to more desired products in the presence of a zeolite. This extra transformation often includes dehydration, decarbonylation, and decarboxylation reactions, leading to an increased production of H₂O, CO, and CO₂, of which the last two are the dominating species in the NCGs. During the catalysed reactions, part of the intermediate compounds is also converted into coke [85] which is mainly deposited on the catalyst. All of the carbon-containing by-products of the catalysed reactions (*i.e.*, CO, CO₂, and coke) are formed at the expense of the compounds in the organic liquid fraction. These considerations are in line with our observations (Fig. 5.2) in which the product yield distribution was considerably influenced by the presence of the catalyst. Compared to the non-catalytic case, a decrease of almost 13 wt.% in the organics yield was seen in the in situ catalytic case, which is associated with an increase in water by almost 5 wt.%, in carbonaceous solids by more than 6 wt.%, and in non-condensable gases by around 4 wt.%. The difference in yields of carbonaceous solids between non-catalytic and in situ catalytic modes can be explained by coke deposition on the catalyst since the char yields in both cases are assumed to be the same.

5.3.3 The effect of successive catalyst regeneration on the product yields

The effect of successive catalyst regeneration was investigated in relation to the mass yields for organics, water, carbonaceous solids, and non-condensable gases as a function of the number of reaction/regeneration cycles (Fig. 5.3). The values obtained from three in situ catalytic experiments with fresh catalyst were averaged and used as reference case (denoted as “R0”). The run with bed materials obtained from the first experiments after regeneration is denoted (R1), with subsequent cycles indicated by R2 to R8. In order to limit experimental errors, two experiments in parallel batches were carried out for every regeneration cycle, and the values were averaged. The experimental conditions and procedures described in sections 5.2.3 and 5.2.4 were also applied for all these tests with regenerated catalysts.

Trendlines in the graphs show clear changes for all products. In comparison with the non-catalytic experiments, a remarkable decrease in the organics yield is observed, *viz.* from 33.2 wt.% to 20.4 wt.% for R0 (fresh catalyst), and further down to 15.8 wt.% for R1 (catalyst one time regenerated). The yield of organics slightly oscillates around 15 wt.% from the second to the sixth regeneration cycle and then starts to increase for the seventh and eighth regenerations to 17.7 and 21.8 wt.%, respectively. This increase in liquid yields in the last reaction/regeneration cycles indicates that with the decreasing activity of the catalyst (see section 5.3.6), the production of a liquid similar to non-catalysed bio-oil is favoured. This results in the convergence of the yields to the non-catalytic values after a certain number of reaction/regeneration cycles. On the contrary, in the presence of fresh ZSM-5-based catalyst (R0) the water yield increases from the non-catalytic level of 18.7 wt.% to 23.4 wt.% as discussed before in Section 5.3.2. The increase in water yields over the zeolites is expected as a result of more intense deoxygenation of the pyrolysis vapours [132]. When the number of

catalyst regenerations is increased, the water yield becomes slightly higher until the sixth regeneration (R6) to 27.2 *wt.%* and then starts to decrease again in the seventh and eighth regenerations to 26.1 and 22.7 *wt.%*, respectively. These opposite trends of the organics and water yields together indicate that the deoxygenation via H₂O production passes through a maximum during successive catalyst regeneration, returning at the end (after six cycles) in the direction of the non-catalytic case.

The non-condensable gas yield for the non-catalytic experiments is 25.7 *wt.%* and increases to 29.6 *wt.%* after using fresh catalysts. The highest NCG yield (33.2 *wt.%*) is found after three reaction/regeneration cycles while after this point the yields starts to decrease gradually to a level of 27.7 *wt.%* after the eighth regeneration, which is coming close to the value for the non-catalytic experiments.

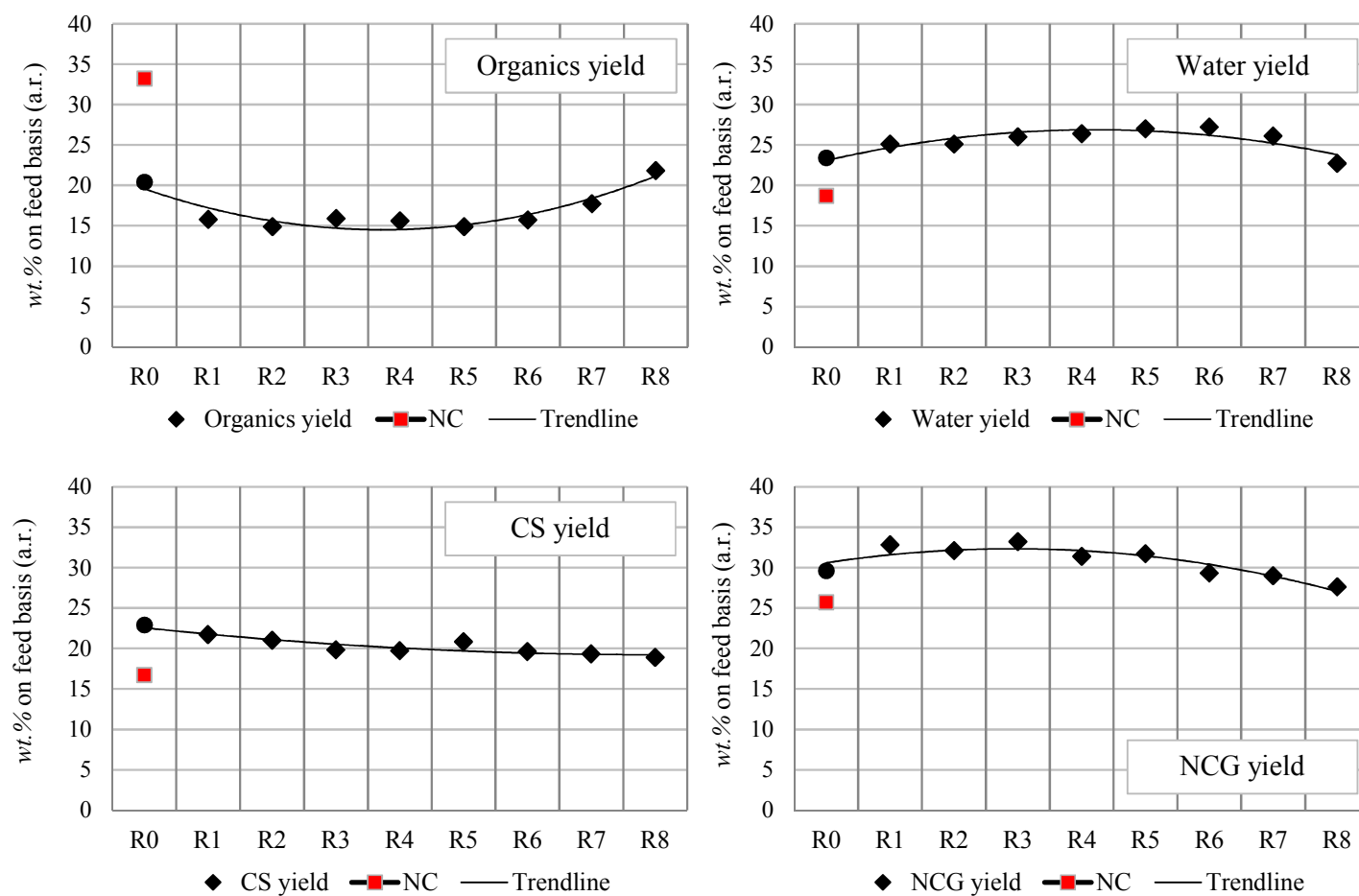


Fig. 5.3. Influence of successive catalyst regeneration (R1 to R8, ◆) on the product yields of pine wood pyrolysis at 500 °C. Results for the non-catalytic (NC, ■) and catalytic pyrolysis with fresh catalyst (R0, ●) are included for comparison.

The individual yields of char and the system deposits were assumed to be *ca.* 12 wt.% and *ca.* 5 wt.%, respectively for all the experiments because each experiment was carried out under identical process conditions. This has been checked a number of times. Besides, the residence time of the pine wood particles in the bed (t_{run}) was always long enough for a complete devolatilization. Hence, the differences in the yields of carbonaceous solids must represent the changes in the coke on catalyst. Fig. 5.4 shows those changes in the coke yield as a function of the reaction/regeneration cycles. Obviously the catalyst pores are blocked by coke (and mineral) deposition, thereby limiting the access to the active surface area of the catalyst. The fresh catalyst gives a coke yield of 6.2 wt.%. The coke yield then steadily decreases to a level of 2.2 wt.% after the eighth regeneration. Assuming that the regeneration procedure is efficient in burning off all the coke, it is evident that coke is always formed again after each regeneration step. If the coke formation is taken as an indication of the catalyst activity, the steady decrease in coke on catalyst over the eight reaction/regeneration cycles would point at a gradually decreasing catalyst activity, which is in line with the observations regarding the product yields (Fig. 5.3).

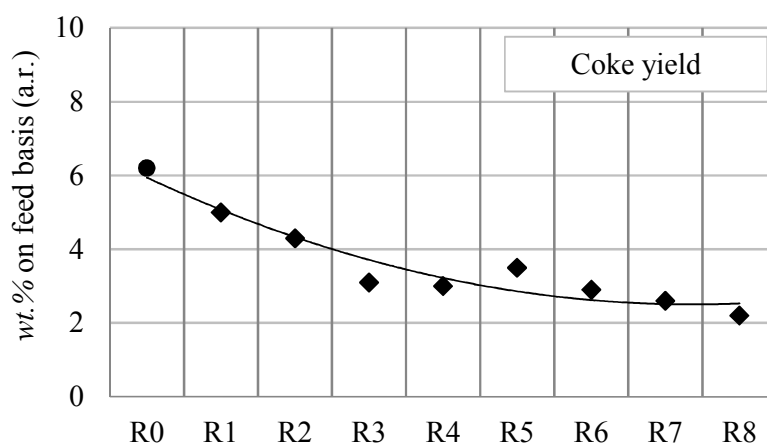


Fig. 5.4. Changes in the coke-on-catalyst (heterogeneous coke) yield along the successive catalyst regeneration cycles. R1 to R8, ◆: experiments with pine wood at 500 °C. R0, ●: in situ catalytic fast pyrolysis with fresh catalyst.

5.3.4 The effect of successive catalyst regeneration on the deoxygenation of pyrolysis vapours and the energy density of bio-oils

The main goal of catalytic pyrolysis is to upgrade the highly oxygenated pyrolysis vapours by removal of the oxygen, and the cracking/rearrangement of molecules, in order to produce a liquid product rich in alkanes and aromatics [195]. The elemental distribution of the various pyrolysis products obtained after all the reaction/regeneration cycles (R1 to R8), as well as those for the non-catalytic (NC) and fresh catalyst cases (R0), were collected in Table A.5.2 of the Supporting Information. CO, CO₂, and H₂O are the primary products of bio-oil oxygen removal in zeolite catalytic upgrading [85], and their yields are given in Table 5.3. Being the main components of the non-condensable gases, CO and CO₂ yields exhibited a trend similar to one observed for the NCG yields (see Fig. 5.3). The non-catalytic CO yield of 13.0 wt.% increased to 16.2 wt.% for pyrolysis with a fresh catalyst, and reached a maximum

of 18.7 wt.% for pyrolysis after the first regeneration, before dropping to a value of 14.9 wt.% for pyrolysis after the eighth regeneration. Despite some minor differences, the CO₂ yields overall followed the same trend. In accordance with the literature, these results indeed confirmed that decarbonylation and decarboxylation, together with dehydration (Fig. 5.3), are the main mechanisms for bio-oil deoxygenation in catalytic pyrolysis with zeolites.

Table 5.3. Yields of CO, CO₂, and H₂O in wt.% on feed basis (a.r.), elemental composition of bio-oil (wt.% in dry bio-oil basis), and the bio-oil heating value (wt.% in dry bio-oil basis) listed for all successive reaction/regeneration cycles (R0 to R8) and the non-catalytic case^a (NC).

	CO	CO ₂	H ₂ O	C	H	O	HHV (MJ kg ⁻¹)
NC	13.0 ± 0.8	10.0 ± 0.7	18.7 ± 1.0	60.1	5.8	34.1	22.5
R0	16.2 ± 1.7	10.1 ± 1.1	23.4 ± 2.4	70.1	5.7	24.2	27.4
R1	18.7 ± 0.8	11.4 ± 0.4	25.1 ± 0.9	75.1	5.6	19.3	29.9
R2	17.9 ± 1.2	10.7 ± 0.8	25.1 ± 3.3	77.3	5.3	17.4	30.5
R3	18.5 ± 1.2	11.3 ± 0.6	26.0 ± 2.6	76.4	5.1	18.5	29.8
R4	17.1 ± 1.5	11.1 ± 0.8	26.4 ± 4.3	75.6	5.2	19.2	29.5
R5	16.9 ± 1.6	11.7 ± 0.1	27.0 ± 2.8	77.2	4.8	18.0	29.6
R6	16.0 ± 2.2	10.6 ± 1.3	27.2 ± 1.5	76.4	4.4	19.3	28.5
R7	15.8 ± 0.5	10.0 ± 0.1	26.1 ± 0.1	74.4	5.0	20.6	28.6
R8	14.9 ± 0.3	9.7 ± 0.5	22.7 ± 0.6	66.4	5.5	28.2	25.2

^a Experiments with pine wood at 500 °C.

Table 5.3, further shows that the elemental yields (wt.% in dry bio-oil basis) of carbon and oxygen in bio-oil show opposite trends with respect to each other. The bio-oil carbon content passes through a maximum, while the oxygen content passed through a minimum with an increasing number of reaction/regeneration cycles. The maximum carbon content of the bio-oil was 77.3 wt.% after two regeneration cycles (R2), and the lowest oxygen content was observed in R2 with a value of 17.4 wt.%. The hydrogen contents in the produced bio-oils were only slightly affected by the number of catalyst regeneration cycles. On average the hydrogen content after every regeneration decreased with 10–20 % in comparison to the non-catalytic case (5.8 wt.%), and a minimum was observed after five to six regenerations. As an illustration of the maximal catalytic effect one could compare the chemical formula that can be derived from the elemental composition listed in Table 5.3, for the non-catalytic pyrolysis (NC) with the one for catalytic pyrolysis after five regenerations (R5). It changes from CH_{1.16}O_{0.43} to CH_{0.75}O_{0.17}, respectively. Apparently, the catalyst is effective in rejecting oxygen from the organics phase at the expense of hydrogen. The change in elemental composition can also be clearly seen in the heating value of the product oil (dry bio-oil basis), which increased from 22.5 MJ kg⁻¹ for the non-catalytic case (NC) to a value of approximately 30 MJ kg⁻¹ after 1–5 regenerations. Despite this remarkable increase, the energy density of the produced bio-oil was still low compared to the energy density of conventional fuels [30]. In attempt to summarize the observations collected in Table 5.3, one

could say that the catalyst activity increases over the first two to three reaction/regeneration cycles, and then maintains its activity over a number of following cycles, but finally loses part of its activity over the last two cycles R7 and R8. However, even after eight cycles, some catalyst activity was still clearly observable from the increased carbon monoxide and water production, the higher carbon and the lower oxygen contents of the product oil organics, and the corresponding rise in heating value.

Fig. 5.5 shows the changes in CO_x yields (sum of CO and CO_2 yields), the CO/ CO_2 ratio, and the changes in the yields of H_2 , CH_4 , and C_{2+} as a function of the increasing number of catalyst regenerations.

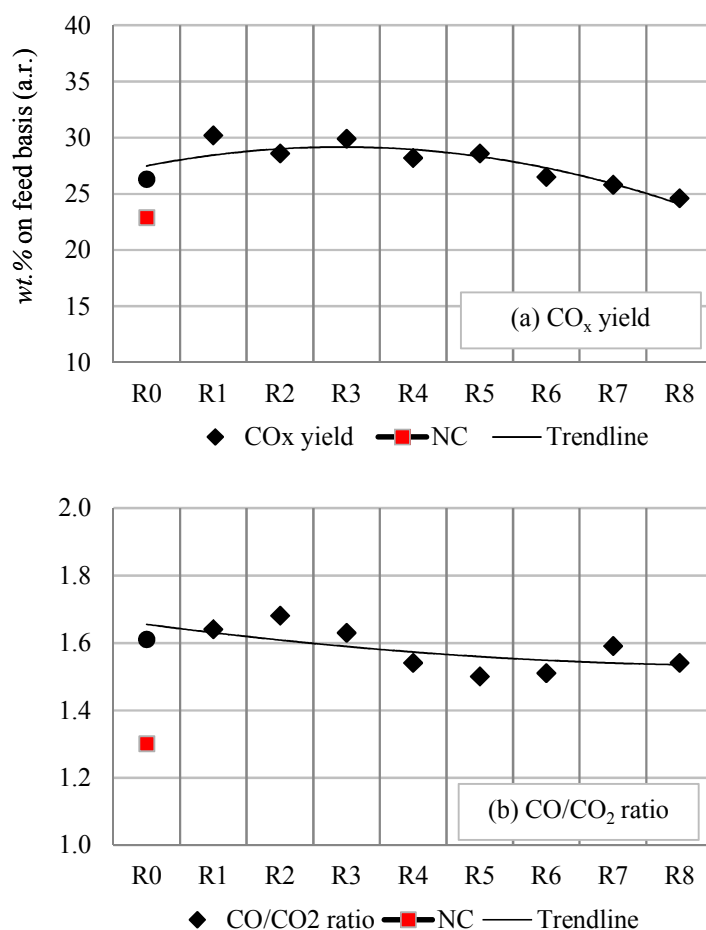


Fig. 5.5. Changes in (a) CO_x yield (the sum of CO and CO_2), (b) CO/ CO_2 ratio, (c) CH_4 yield, (d) C_{2+} yield (sum of C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8), and (e) H_2 yield, obtained after successive reaction/regeneration cycles (R1 to R8, \blacklozenge). The result of non-catalytic (NC, \blacksquare) and catalytic fast pyrolysis with fresh catalyst (R0, \bullet) are included for comparison. Catalytic pyrolysis experiments of pine wood at 500 °C.

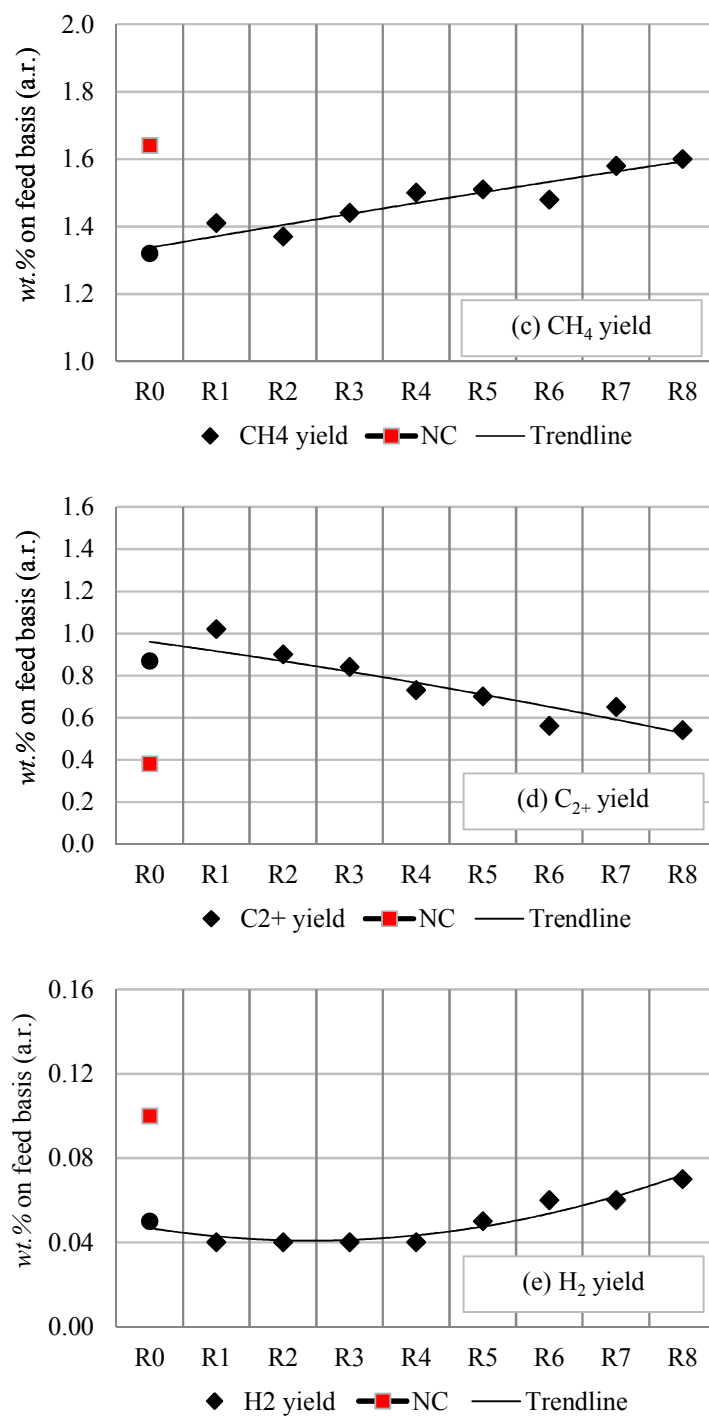


Fig. 5.5. *continued.*

The trend of the CO_x yield shown in Fig. 5.5a, was similar to the one for the NCG yield shown in Fig. 5.3. It showed the highest level of approximately 30 wt.% in the beginning and then a gradual decrease to a value of 24.6 wt.%, which is quite close the non-catalytic value of 22.9 wt.%.

The CO/CO₂ ratio of the product gases is assumed to be a good measure to monitor the catalytic activity [76]. In Fig. 5.5b, the CO/CO₂ ratio was shown to increase from a value of 1.3 for non-catalytic pyrolysis to 1.6 for pyrolysis in the presence of the fresh catalyst (R0). The trend was then slightly downward, *viz.*, to a value of about 1.54 after eight cycles. Apparently, the presence of catalyst favours the decarbonylation mechanism over the decarboxylation mechanism during all the successive reaction/regeneration cycles. Remarkable was the single oscillation in CO/CO₂ between a maximum value of 1.68 and a minimum value of 1.50.

The CH₄ yields decreased from a non-catalytic value of 1.64 wt.% to the value of 1.32 wt.% in R0 when the catalyst was added (Fig. 5.5c). Then, in a slightly fluctuating way, it steadily increased to the value of 1.60 wt.% after eight regenerations (R8), close to the value for the non-catalytic pyrolysis. On the contrary, the C₂₊ yield (C₂H₄ was being the most abundant hydrocarbon) jumped to a peak value of 1.02 wt.% in R1 and then started to decrease steadily to a value of 0.54 wt.% in R8 (Fig. 5.5d). This could be due to the gradual increase of biomass ash along the reaction/regeneration sequence. The presence of ash likely promoted alkane production at the expense of alkenes. The higher level of C₂₊ yield in catalytic pyrolysis was likely caused by secondary cracking of heavier molecules to lower molecular weight hydrocarbons.

Fig. 5.5e shows that on a weight basis H₂ seems to be a nondominant by-product both in non-catalytic and catalytic pyrolysis. However, it is interesting to note that in the presence of the ZSM-5-based zeolite catalyst, the yield of H₂ is decreased by half (from 0.1 wt.% to an average of 0.05 wt.%). During the first four reaction/regeneration cycles, its value remained unchanged after which it slowly increased to the non-catalytic value. Apparently, in catalytic pyrolysis H₂ is consumed, which may contribute to the formation of hydrocarbons (dehydration reactions). While overlooking the results collected in Fig. 5.5, it seems that the trends of the yields of individual non-condensable gas compounds are a good indicator of the catalyst deactivation, and it may be worthwhile to investigate such correlations in future investigations. Regarding the reduced hydrogen and methane yields observed for catalytic pyrolysis, this cannot be explained from a possible occurrence of the water gas shift reaction and/or methane reforming in the vapour phase. Methane is stable under the applied conditions, while the water gas shift reaction (in the presence of biomass minerals and the ZSM-5-based zeolite catalyst) would have resulted in an increase of hydrogen production while the carbon monoxide yield would have expected to decrease, which is not in line with the observations. Although the reasons for the reduced hydrogen and methane production remain unclear in this stage of research, it definitely is beneficial if all, or part of the hydrogen lost from the non-condensable gases is preserved in the produced bio-oil.

5.3.5 The effect of successive catalyst regeneration on the bio-oil quality

Fig. 5.6 shows the yield variations of the measured compounds using the GC×GC/MS-FID. The latter are being classified according to their functional group, and as a function of the number of catalyst regeneration cycles. The compounds were grouped as sugars, aldehydes, acids, furans, ketones, phenols, aromatics and others (unclassified oxygenates). Table A.5.3 (in the Supporting Information) shows the details of the most prevalent individual compounds detected via GC×GC-TOF-MS analysis and quantified by GC×GC/MS-FID. For the quantification procedure, the reader is referred to the paper of Djokic *et al.* [180]. It should be taken into account that the yields shown in Fig. 5.6 and Table A.5.3 were normalized and expressed relative to the as-received feed basis.

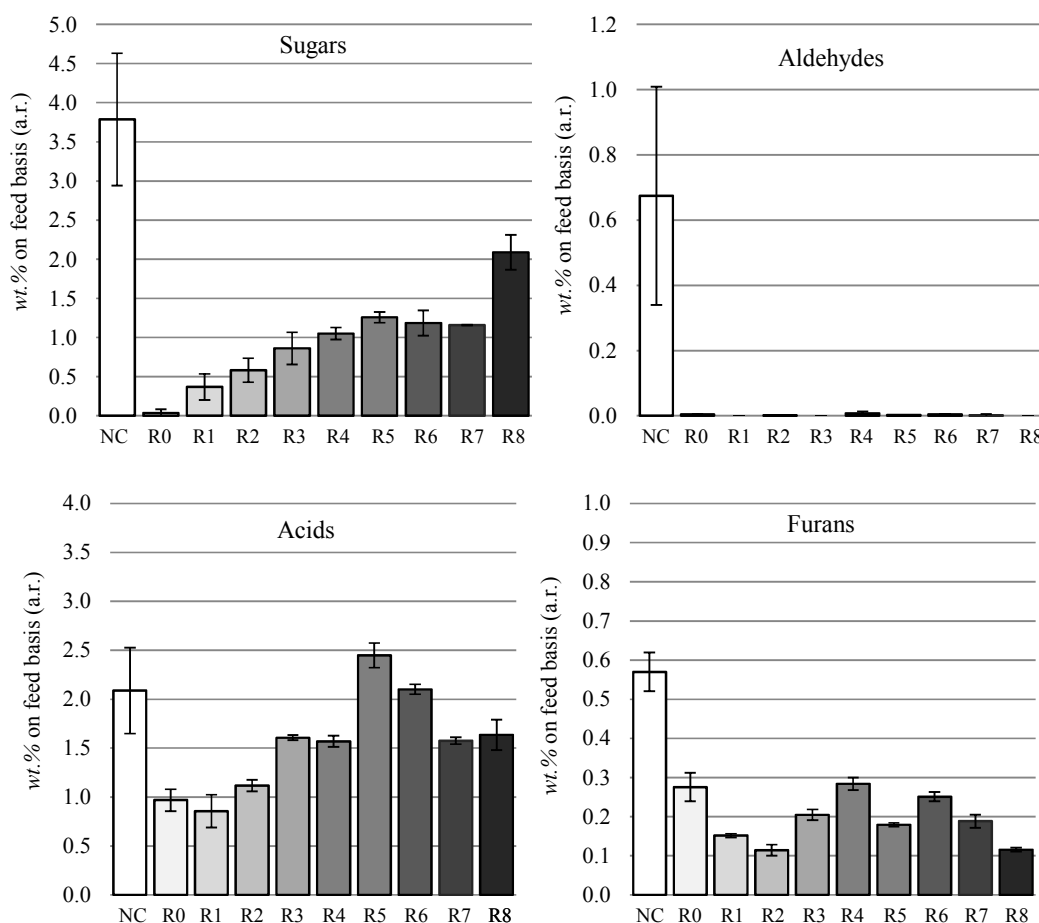


Fig. 5.6. Results of pine wood experiments at 500 °C. Changes in bio-oil composition for successive reaction/regeneration cycles (R1 to R8). Bio-oil constituents were grouped according to their chemical functional groups (GC×GC/MS-FID detectable only). NC refers to non-catalytic pyrolysis as a reference case. R0 indicates catalytic fast pyrolysis with fresh catalyst. The yields are shown in wt.% on feed basis (a.r.). Error bars represent standard deviations.

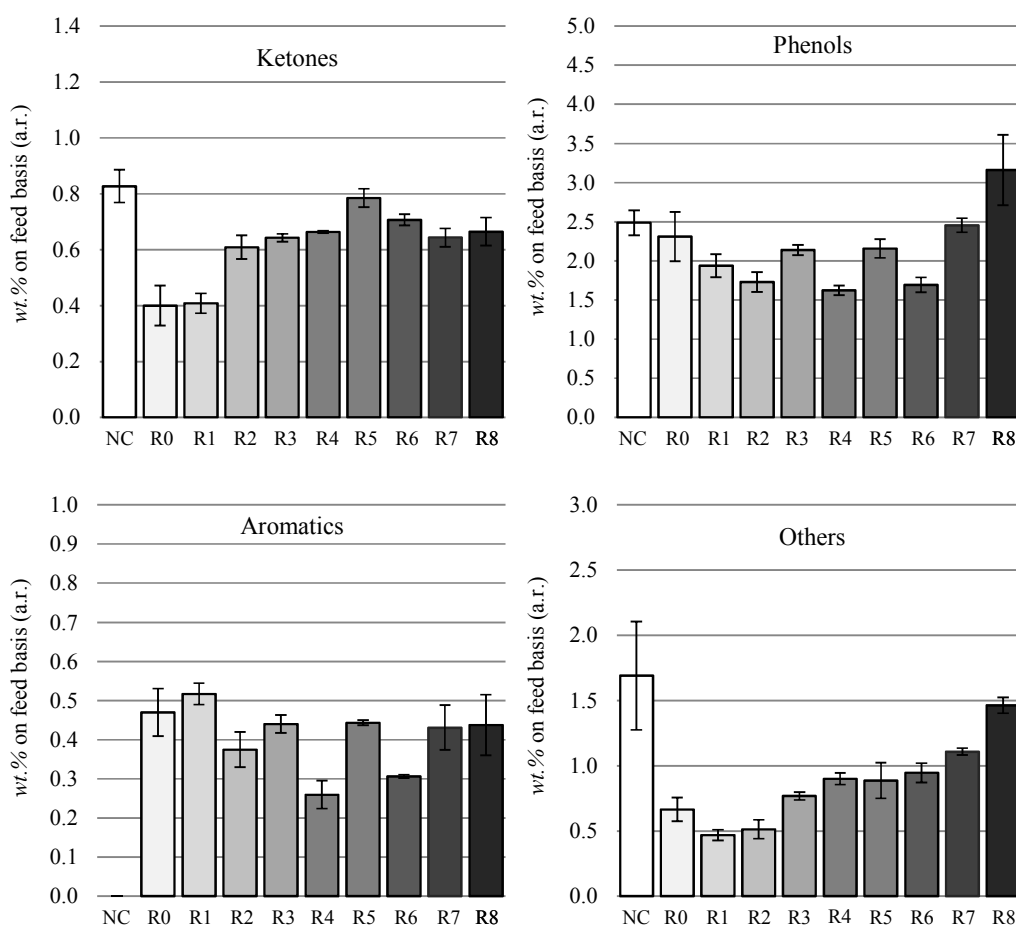


Fig. 5.6. *continued.*

In bio-oil from non-catalytic pine wood pyrolysis, sugars constitute a high portion, and a mass fraction percentage of approximately 3.8 wt.% was found by GC×GC/MS analysis. The most abundant sugar compound was levoglucosan with more than 3 wt.% (Table A.5.3 in the Supporting Information). In the presence of fresh catalyst, the amount of sugars was significantly reduced, and levoglucosan could not be observed anymore. This suggests that the amount of catalyst in the reactor bed is enough to retain its catalytic activity throughout the entire experimental run time. As the number of reaction/regeneration cycles increased, the quantity of sugars in bio-oil steadily rose again but without reaching the original level of the non-catalytic case. Although clearly present in the oil from non-catalytic pyrolysis, aldehydes (particularly hydroxyacetaldehyde) were completely undetectable when using fresh catalyst, as well as after any of the subsequent reaction/regeneration cycles. The quantity of detectable acids decreased during pyrolysis in the presence of a fresh catalyst (R0) by more than a factor 2. However, this effect largely disappeared again after repeated regeneration. Obviously acetic acid, the main detectable compound, was quite stable under the applied conditions. As concluded already in the previous subsection (increased CO/CO₂ ratio in the non-condensable gas), apparently the decarbonylation of particularly aldehyde functions is easier than the decarboxylation of acids.

Fig. 2.5 (can be found in Chapter 2 in this thesis) shows the reaction chemistry for the catalytic fast pyrolysis of biomass over a solid acid catalyst. In pyrolysis, furans are produced from the dehydration of hemicellulose as well as by acid catalysed dehydration, decarbonylation, and decarboxylation of anhydrosugars. Produced furans are then converted to hydrocarbons and coke. Just like unsaturated compounds, furans produce large amounts of coke, which rapidly deactivates the zeolites [48]. The reason for the reduced levels of furans in Fig. 5.6 was that most of the furans are converted to hydrocarbons to form monoaromatic hydrocarbons, olefins, and coke. The quantity of ketones decreased by half in catalytic pyrolysis with the fresh catalyst (R0). After the second regeneration, however, ketones started to increase and stayed roughly constant along the subsequent regeneration cycles but always at a level below that of non-catalytic pyrolysis. While almost no aldehydes and sugars (and only minor amounts of ketones) were present in bio-oil obtained when using fresh catalyst, sugars and ketones increased notably after the catalyst had been regenerated. Although the literature suggests [142,208] that this would lead to an increased oxygen content and a reduced stability, Table 5.3 shows that the oxygen content of the produced bio-oil stays at a low level during many of the successive reaction/regeneration cycles.

Phenols are the result of a competition between their formation from lignin and their conversion to monoaromatic compounds (MAHs). They are supposed to originate from lignin depolymerisation mainly. In the presence of acidic zeolites, phenols yield MAHs by (acid catalysed) dehydration, decarbonylation, and decarboxylation reactions. Besides, a considerable amount of phenols is lost due to coke formation (Fig. 2.5, in Chapter 2). Hence, the performance of an acidic zeolite catalyst is directly related to the conversion rate of phenols to MAHs and coke. In Fig. 5.6, a fluctuating trend around 2 wt.% is observed until R6. In R7 and R8, the amount phenols increased remarkably up to 2.5 wt.% and 3.2 wt.%, respectively, the last value being even higher than for the non-catalytic pyrolysis case. All this shows that, as a consequence of increasing catalyst deactivation, the formation of phenols is gradually getting dominant over their conversion to monoaromatics.

In the non-catalytic bio-oil no aromatics were detected. In the presence of the catalyst, aromatics production was favoured but the amount was not consistently affected by the number of catalyst regenerations. Even in the last cycle (R8), similar quantities of aromatics were produced if compared to pyrolysis with the fresh catalyst. This shows that the catalyst remained active in terms of aromatics production. In the case of acidic zeolites such as ZSM-5, some of the heavy oligomers are cracked to light organics (mainly oxygenated), which may then deposit on the catalyst surface and act as coke precursors [209]. Indeed, the major competing reaction to the formation of aromatics is the coke formation inside the zeolite particles, leading eventually to catalyst deactivation. In order to overcome this, fresh/regenerated catalyst would need to be fed continuously to the pyrolysis reactor, while spent catalyst is removed and regenerated in a separate vessel [92].

Other compounds detectable in the bio-oil were the unclassified ones, of which 1-hydroxy-2-propanone was the most abundant one. The yield of these compounds dropped by almost 70 % when going from the original non-catalytic case to the one of the fresh catalyst, and then increased again to the non-catalytic level over all the subsequent reaction/regeneration cycles.

Although the effect varies for the different detectable compound groups, the general picture was that the catalyst activity is adversely influenced by the successive reaction/regeneration cycles. Starting from R0 (fresh catalyst), increasingly more acids, ketones, sugars, and unclassified oxygenates (others) were produced. Depending of course on what had happened to all the GC non-detectable compounds, this would cause the bio-oil to become ever more acidic, less stable, and less well deoxygenated when using a regenerated catalyst. It is obvious that repeated regeneration pushes the yields (always on biomass feed basis) of the various chemical compound groups back in the direction of the values of the non-catalytic bio-oil, with the exception of the phenols and aromatics. The latter are considered to be the compounds with the highest economic value and were still obtained in significant yields after eight regenerations. Clearly, the catalyst was not entirely deactivated and remains active in promoting the cracking of lignin and the subsequent formation of aromatics. Whether or not this would mean that the liquid product after eight reaction/regeneration cycles has, in every respect, a “better” quality than the original, non-catalytic bio-oil depends on its intended utilization and should be the subject of further research.

5.3.6 The effect of successive catalyst regeneration on the surface area of the catalyst

BET surface area analysis has been carried out for spent catalyst/sand mixtures and regenerated catalyst samples because the possible loss of surface area could be an indication of accumulated coke and tar inside the pores. The results are shown in Fig. 5.7.

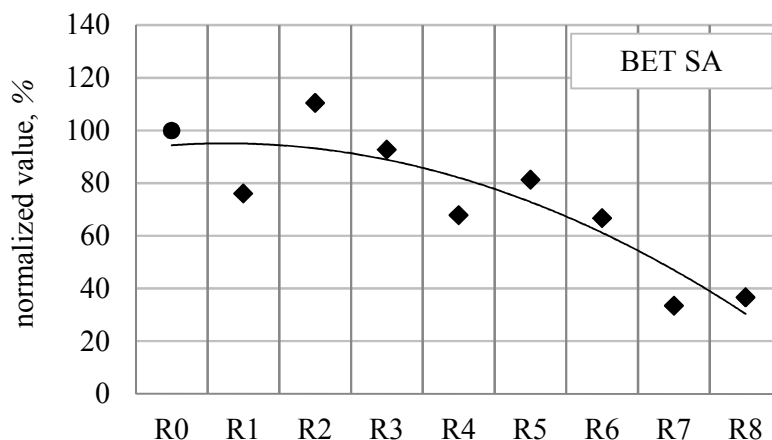


Fig. 5.7. Normalized BET surface area values of ZSM-5-based catalyst for successive reaction/regeneration cycles (R1 to R8, ◆) resulting from experiments with pine wood at 500 °C. The data point for in situ catalytic fast pyrolysis with fresh catalyst (R0, ●) is included for a comparison.

The procedures and conditions applied during the regeneration play a vital role in the performance of the catalyst along the regeneration sequence. Although it was not possible to regain the surface area entirely, a fair retention of surface area was obtained in the first three to five regenerations. However, during the last few cycles the surface area appeared to be reduced drastically. With some fluctuations along the regeneration sequence (a declining trend), the surface area recovery decreased to 37 % in R8. Hence, it can be concluded that successive catalyst regeneration causes a significant loss of the catalyst surface area, which causes partial deactivation. Although the catalyst seems regenerable to a certain extent, and the regeneration procedure was successful for at least a number of cycles, eventually the BET surface area collapses due to an accumulative and permanent coke/ash deposition on the catalyst.

5.4 Conclusions

Non-catalytic and in situ catalytic pyrolysis of pine wood at 500 °C have been examined in a mechanically stirred sand bed reactor to observe the effects of both catalysis and repeated catalyst regeneration, on the pyrolysis products yields and quality. For catalytic pyrolysis, fresh and regenerated ZSM-5-based catalyst particles were mixed with the sand in ratios of about 1:14. After each catalytic pyrolysis experiment, the catalyst was regenerated in air by a programmed temperature procedure reaching up to 600 °C. In total, eight reaction/regeneration cycles were carried out to derive the change in catalyst activity (deactivation) over the increasing number of cycles. The accuracy of the measurements was shown to be high enough for determining clear trends in the yields of the gaseous, liquid, and solid products.

Regarding the yields, it was observed that the values for the produced water, carbonaceous solids, and non-condensable gases in catalytic pyrolysis are all well above (20 to 30 % on the average) the values for the non-catalytic case. However the organics liquid yield is drastically reduced, roughly by a factor two. While looking at the yield trends as a function of the number of reaction/regeneration cycles, they pass through a flat minimum (organics liquid) or maximum (water and non-condensable gases), however, with the exception of the carbonaceous solids whose yield shows a straight, slightly increasing trend. Apparently the catalyst is more active during the first two cycles but clearly loses its activity in the last few cycles. Then, the catalyst regeneration becomes much less efficient, and the yields tend to return to the values of the non-catalytic pyrolysis.

All this was confirmed by the observed yields of the non-condensable gases over the successive reaction/regeneration cycles. Methane and hydrogen productions were clearly suppressed in catalytic pyrolysis, while the formation of carbon monoxide and small hydrocarbons (C_{2+}) was promoted. On a mole basis, *ca.* 90 % of the non-condensable gas consists of carbon monoxide and carbon dioxide. But the course of the methane yield in particular, as a function of the number of reaction/regeneration cycles, seems to be a good indicator of the decreasing catalyst activity (straight increasing trend line, back to the non-catalytic value).

More indications of the catalyst activity were found in the results of the bio-oil GC/MS analysis. The most pronounced effect of catalysis is in the disappearance of sugars and aldehydes. For most of the detectable compounds (sugars, acids, ketones, unclassified oxygenates), values decrease initially in the first few reaction/regeneration cycles but then climb again to the non-catalytic values. Aromatics (not detected in the case of non-catalytic pyrolysis!) are being produced over the entire series of reaction/regeneration cycles, showing that the catalyst maintains its activity with respect to these, possibly valuable compounds.

The catalyst activity was further explored by BET surface analysis which indeed revealed a decrease in the surface area over the last four reaction/regeneration cycles. The final fraction left is just 37 % of the original BET surface area. In agreement with this reduced catalyst activity potential seems to be the measured coke-on-catalyst, which decreases from 6 to 2 wt.% of the biomass feed.

It finally appeared that the energy lost in the non-condensable gases and carbonaceous solids (by-products) is significant. While in the non-catalytic pyrolysis case 58 % of the energy was retained in the bio-oil, this was reduced to around 45–48 % in the worst cases of catalytic pyrolysis, *viz.*, after 1–4 catalyst regenerations.

Although multiple, full regeneration of the ZSM-5-based zeolite catalyst appeared impossible, its activity with respect to the production of aromatics and phenols was largely maintained over a series of eight reaction/regeneration cycles. Although beneficial effects of catalysis were observed, obviously the conditions for catalytic pyrolysis were suboptimal. New catalyst formulations, vapour phase treatment instead of in situ catalysis (*ex situ* processing mode), improved catalyst regeneration procedures, application of other temperatures, and optimization of space velocities are all possible strategies to further improve the result of catalytic fast pyrolysis of biomass.

Chapter 6

Effect of biomass ash in catalytic fast pyrolysis of pine wood

Abstract

Fast pyrolysis experiments of pine wood have been performed in a continuously operated mechanically stirred bed reactor at 500 °C. The effects of the pine wood ash were studied by comparing non-catalytic and catalytic experiments (using a ZSM-5 based catalyst) with their ash-added counterparts. To show the case of ash accumulated from the biomass feeding, the results of catalytic fast pyrolysis obtained after eight reaction/catalyst regeneration cycles were included as well. The objective was to distinguish between the ash-catalyst interactions and the catalyst deactivation. The latter may be caused by thermo-mechanical, chemical and/or structural changes in the catalyst; such as poisoning, fouling, dealumination, and attrition, as well as by coke deposition. Ash concentrations up to ca. 3 wt.% relative to the amount of pine wood fed, and ca. 0.002 wt.% relative to the amount of bed material, were found to be sufficient to change the distribution and the composition of pyrolysis products. The addition of ash to the catalytic fast pyrolysis, caused a reduction in the yields of both the organics and coke by 2 wt.% (on feed basis), while increases of 1 wt.% and 4 wt.% in the water and non-condensable gases were observed, respectively. The total yield of CO plus CO₂ was boosted by more than 10 %, while the CO₂ production (decarboxylation reactions) was favoured clearly. Moreover, the presence of added-ash suppressed the conversion of sugars and acids –these were more pronounced in the case of accumulated-ash– as well as of the phenols. The catalyst deactivation during the reaction/regeneration cycles is not only related to the presence of ash but also to changes in the structure and composition of the catalyst. To overcome the drawbacks of biomass ash in catalytic fast pyrolysis, either the biomass feedstock has to be leached (ash removal) before being introduced to the process, or the char (which contains a vast majority of the biomass ash) has to be physically removed from the catalyst before the regeneration step.

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6.1 Introduction

Lignocellulosic biomass is an abundantly available, renewable resource of organic carbon and can be transformed into energy-dense alternative liquid fuels through fast pyrolysis. Fast pyrolysis is the thermal decomposition of the natural polymeric constituents of biomass in an oxygen-free atmosphere at temperatures around 500 °C. At optimal conditions, including high heating rates of the biomass particles, short vapour residence times and fast condensation of pyrolysis vapours, high yields of pyrolysis liquid (usually in the range of 60 to 70 wt.%, dry-feed basis) can be achieved.

However, some adverse properties of pyrolysis liquid limit its use in chemicals production and fuel applications. These include its high water content (15–30 %), oxygen content (35–40 wt.%), corrosiveness (pH of 2–3), relatively low heating value compared to fossil fuels (*ca.* 17 MJ/kg), poor volatility, and high viscosity. Hence, the quality of pyrolysis liquids must be improved before they can be considered as a liquid feed in the production of heat, electricity, transportation fuels and chemicals [29]. Catalytic fast pyrolysis (CFP), which is based on the use of heterogeneous catalysts in the fast pyrolysis process, intends to improve the quality of the liquid by steering the vapour phase reactions with respect to rates and selectivity.

In a CFP process, the inert heat transfer material is (partially) replaced by a solid catalyst. The presence of catalyst favours oxygen removal via decarbonylation (CO rejection), decarboxylation (CO₂ rejection) and dehydration (H₂O formation) reactions. The ultimate composition of the produced liquids is influenced by factors such as the type of the biomass feedstock, the type of the catalyst (including pore size, acidity, nature of active sites and the presence of metals), optimal operating temperature of the catalyst, and the catalyst-to-feed ratio. In addition, the interaction between the volatiles generated by fast pyrolysis and the bed contents (*e.g.* catalyst, char, and ash) is an important feature of the pyrolysis reactor. More specifically, this interaction refers to reactions of reactive species present in the volatiles (including radicals generated by thermal cracking) with the char/ash particles [210]. Obviously, the selected catalyst should play a vital role in suppressing the production of undesirable oxygenated compounds (acids, sugars, poly-aromatic hydrocarbons, *etc.*) while promoting the production of value-added compounds (phenolics, alkanes, mono-aromatic hydrocarbons, *etc.*). Regarding the corresponding removal of oxygen, the preferred route from both, an energy-yield point of view and the desire to maintain a relatively high H/C ratio, must be decarboxylation [100,147].

One of the problems encountered in CFP is the deactivation of the catalyst which implies the physical, chemical, thermal, and mechanical degradation of the catalyst leading to a reduced activity and selectivity [198]. In CFP, deactivation mainly occurs by the deposition of coke and metals on the catalyst which can poison the active sites of zeolites or block the pores [200]. Accumulation of ash on or inside the catalyst could also be responsible for catalyst deactivation, as it is reported that biomass originated alkali and alkaline earth metals (AAEMs) can poison the catalyst [29]. Like in conventional FCC (fluid catalytic cracking) processing, the catalysts deactivated by coke can be reused in a CFP process after being regenerated. In FCC regeneration, the catalyst is subjected to high temperature oxidative

treatment to burn the coke off from the catalyst and thereby (partially) restore its activity [126]. In biomass CFP however, the coke-on-catalyst contains more oxygen and hydrogen than the coke-on-catalyst obtained in FCC processing. Regeneration of the catalysts thus yields water, apart from only CO_x ($\text{CO} + \text{CO}_2$), which for ZSM-5 and similar structured catalysts could lead to dealumination, and thus loss of active (acid) sites [200,203].

All biomass materials contain ash-forming mineral nutrients in the form of cations which are bound onto the organic matrix of biomass at carboxylic and/or phenolic groups, or in the form of precipitates, such as a salt [211]. These indigenous and catalytically active minerals included in the biomass structure, such as alkali and alkaline earth metals (AAEM species, *e.g.* Ca, K, Mg, and Na), are known to catalyse cracking and several thermolysis reactions in the vapour phase and remould the chemical composition of a resulting pyrolysis liquid, and change the pyrolysis product distribution [12,44,212–215].

To prevent their diverse effects on pyrolysis product quality and distribution, the ash-forming elements can be removed from the biomass to some extent by washing with water, and more extensively by using an acidic washing liquid [216]. The main chemical composition of biomass is sensitive to the leaching conditions wherein harsh leaching can cause the degradation of hemicellulose [167,213]. Leaching also influences the chemical composition of pyrolysis liquid [217]. Even very small quantities of either alkali or alkaline earth metals in their chloride forms were shown to be sufficient to significantly alter the pyrolysis products. The presence of as little as 0.5 wt.% ash led to a strikingly different chemical speciation: in terms of levoglucosan yield, the order of strong to modest influence was found to be $\text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ [212].

While the conclusions concerning the effects of inorganic minerals on non-catalytic pyrolysis are well known, only few literature studies are available regarding the effects of ash and its constituents on the CFP of biomass. As of today, various projects have tried/are trying to push catalytic fast pyrolysis to the pilot scale or even to the commercial scale and have met varying levels of success. Moreover, most of the studies in CFP literature concern the use of fresh catalyst; whereas, in large-scale practical applications, the spent (and coked) catalyst is regenerated (subjected to combustion) to be returned to the pyrolysis process [50]. Although, this is pretty much similar to the FCC process in an oil refinery, one aspect that is different – and thus, far not properly understood – is that biomass also contributes mineral matter (or ash) to the process. Through successive cycles of pyrolysis and catalyst regeneration, a considerable amount of this ash accumulates and could potentially affect the chemistry of pyrolysis as well as the stability and/or the activity of the catalyst. Mullen *et al.* [218] examined the accumulation of Ca, Cu, Fe, K, Mg, Na, and P from switchgrass on HZSM-5 during the catalytic pyrolysis in a fluidized bed reactor. The total amount of these elements was observed to be accumulated on HZSM-5 in a linear fashion during the successive use of the same catalyst sample. The catalytic activity, as measured by a drop in deoxygenation of the pyrolysis oil products and in selectivity of aromatic hydrocarbons, was decreased concurrent with the increase in inorganic elements on the HZSM-5. They concluded that some factors such as catalyst attrition could contribute to the decrease in catalytic activity, and the reactor designs decreasing the exposure of the raw biomass with the catalyst would be beneficial to catalyst lifetimes. Paasikallio *et al.* [219] performed the CFP of pine sawdust in

VTT's Process Development Unit with a biomass throughput capacity of 20 kg h⁻¹. A spray dried HZSM-5 catalyst was used. The changes in product yields, physical and chemical properties of the CFP products, and the changes in the properties and the structure of the catalyst were observed during a continuous run of over four days. Coke formation on the catalyst was observed to be heaviest at the beginning of the experiment, but then subsided over time. Catalyst micropore area and volume also decreased during the experiment; these were accompanied by apparent changes in the crystallinity and the structure of the catalyst. Biomass alkali metals (Ca, K, Mg, P, *etc.*) deposited on the catalyst in time, and a linear correlation was observed between this phenomenon and the decrease in the acidity of the catalyst.

To understand the role of indigenous or added inorganic compounds in CFP of biomass, and the potential ash/catalyst interactions that may take place in CFP, the influence of them on the distribution and composition of products resulting from the primary and secondary fast pyrolysis reactions has to be examined. Parameters such as the type and the condition of the catalyst, and the presence of inorganic constituents in the biomass, could be used to alter the relative rates of the biomass decomposition and subsequent vapour phase reactions, and eventually produce pyrolysis liquids with an improved composition. Fig.1 shows the possible effects of the presence of the ash (whether or not accumulated during the process) on the activity of the catalyst in catalytic fast pyrolysis of biomass. Hypothetically, four different pathways can be distinguished on how the ash influences the vapour phase chemistry and the activity of the catalyst. It should be noticed that combined effects are possible too.

- 1) The catalytic effect of ash itself on the primary pyrolysis vapours results in the increased production of non-condensable gases (NCGs) and char;
- 2) Ash may crack some larger vapour phase molecules inaccessible to the catalyst's interior, to smaller ones which are capable of entering the catalyst pores;
- 3) Cracked vapours may then either be further reformed by the catalyst (a) or not (b)
- 4) Ash particles poison the catalyst and (negatively) affect the vapour conversion and the reaction chemistry.

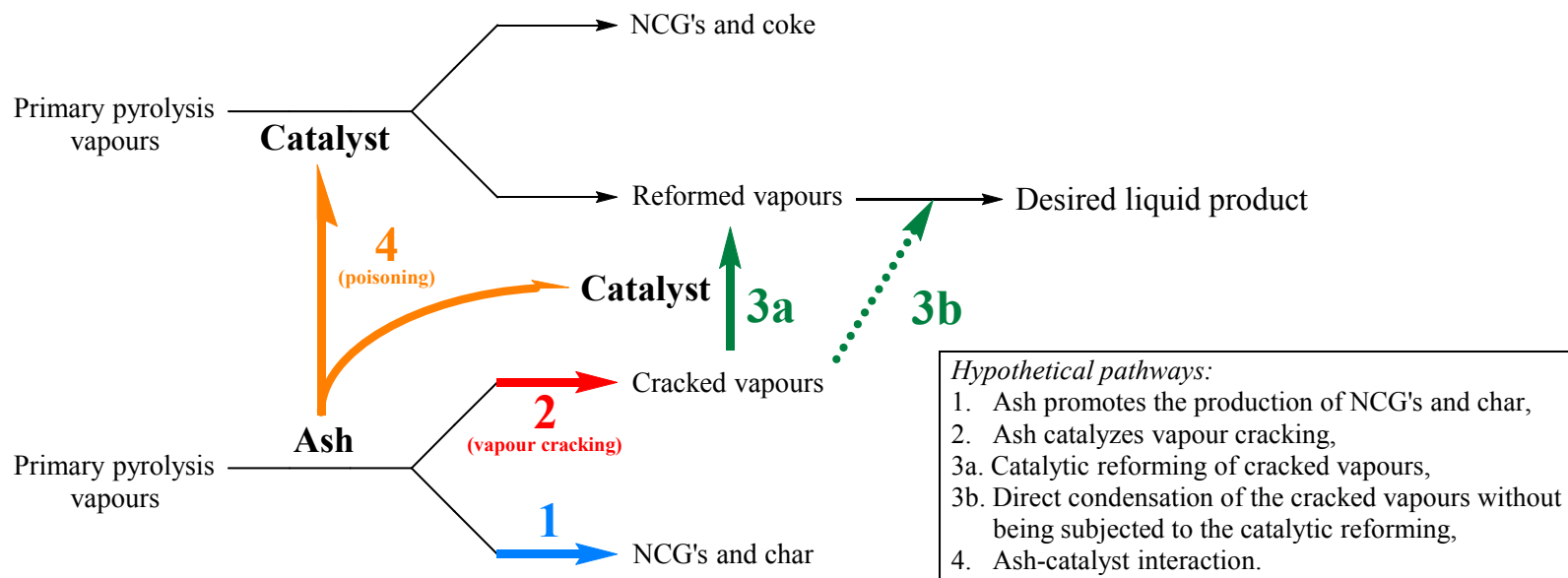


Fig. 6.1. Possible impact of ash on the catalyst and on the products in catalytic fast pyrolysis of biomass.

The objective of this paper is to investigate the effects of indigenous and/or added biomass ash and its major constituents on the pyrolysis product yields and composition as observed in the non-catalytic and catalytic fast pyrolysis of pine wood. A discussion is provided on whether catalyst deactivation is caused merely by coke deposition and thermo-mechanical, chemical and structural changes of the catalyst, or by the presence of the biomass ash as well. The biomass ash could impact the catalyst properties directly (poisoning) or affect the pyrolysis vapours reaction pathways. For this purpose, non-catalytic and catalytic (in situ) fast pyrolysis experiments have been carried out with a ZSM-5 based catalyst in a laboratory scale, mechanically stirred bed reactor. The results of these experiments were compared with those of their pine-wood-ash added counterparts, and with the findings of an experiment in which the catalyst was successively reacted and regenerated eight times while the ash was accumulating in the bed material.

6.2 Experimental

6.2.1 Materials

In the experiments, pine wood (Bemap Houtmeel B.V., Bemmelen, The Netherlands) was used as the reference biomass feedstock. Prior to the experiments, this feedstock was sieved to a particle size of 1-2 mm. The moisture and ash contents were 7.5 wt.% and 0.3 wt.% (on as-received basis, a.r.), respectively. The proximate analysis data, the elemental composition and the higher heating values (in as received and dry basis) of the pine wood are listed in Table 6.1.

Biomass ash was obtained by burning the pine wood at 600 °C in air. The chemical composition of ash obtained from pine wood is shown in Table 6.2. Calcium was found to be the major constituent in the ash (45 wt.%). Other major constituents were potassium (20 wt.%), manganese (9 wt.%) and magnesium (7 wt.%). The majority of the AAEMs present in the structure of biomass are reported to be in the form of water soluble salts such as chlorides, nitrates, carbonates and phosphates [220].

Silica sand (PTB-Compaktuna, Gent, Belgium) with a mean diameter of 250 μm and a particle density of 2650 kg/m³ (compacted bulk density = 1660 kg/m³) was used as the bed material in the non-catalytic experiments and blended with the catalyst and/or with the ash in the catalytic fast pyrolysis and ash addition experiments.

Table 6.1. Properties of pine wood.

Proximate analysis (wt.%)	
Fixed carbon (d.b.)	14.96
Volatiles (d.b.) [ASTM E872-82]	84.76
Moisture (a.r.) [ASTM E871-82]	7.52
Ash (d.b.) [ASTM E1755-01]	0.33
Ultimate analysis (d.b.) [wt.%]	
C	47.1
H	5.9
O	46.4
N	0.04
S	0.06
Alkali metals (d.b.) [mg/kg]	
K	346.2
Na	10.1
Mg	112.8
Ca	767.0
HHV (a.r.) [MJ/kg] ^a	16.91
HHV (d.b.) [MJ/kg]	18.29

d.b.: dry basis

a.r.: as received basis

^a Calculated by using the Milne formula [187]**Table 6.2.** Chemical composition of ash obtained from pine wood, (d.b.) [wt.% in ash].

<i>Element</i>	<i>wt.%</i>	<i>Element</i>	<i>wt.%</i>
Ca	44.6	Ti	0.2
K	20.1	Pb	0.2
Mn	9.2	B	0.1
Mg	6.6	Cu	0.1
Si	5.6	Ni	0.03
S	3.3	Sn	0.02
Al	2.3	Cd	0.02
Fe	2.0	Cr	0.01
P	2.0	V	0.003
Co	1.4	Li	0.001
Zn	0.8	As	BDL
Ba	0.6	Mo	BDL
Na	0.6	Sb	BDL
Sr	0.2	Se	BDL

BDL: below detection limit

A spray dried heterogeneous ZSM-5 based catalyst, indicated as ‘Type A’, was prepared and supplied by Albemarle Catalyst Company B.V. (Amsterdam, The Netherlands). Physical and chemical properties of this catalyst can be found in Appendix A (this appendix is confidential and can only be accessed by signing a confidentiality agreement). The catalyst was received in the acid form and has been treated by the manufacturer accordingly. Prior to the delivery, this catalyst was calcined in air at 500 °C for 1 h to decrease the moisture content of the catalyst to below 1 wt.%. This was applied to prevent aging in the long term storage of the catalyst. Here, the term ‘aging’ represents the anticipated adsorption of water and/or CO₂ on the catalyst from its contact with air.

6.2.2 Experimental setup and the analysis of pyrolysis products

Non-catalytic and catalytic pyrolysis experiments have been performed in a fully controlled, continuously operated lab-scale setup as shown in Fig. 5.1 (see Chapter 5 in this thesis).

Approximately 100 g of pine wood, at a feed rate of *ca.* 1.7 g·min⁻¹, is fed during every run, which could be determined by measuring the mass difference between pine in the storage hopper and in the feeding screw, before and after each experiment. A pyrolysis temperature of 500 °C and a total inert gas (N₂) flow rate of *ca.* 160 L h⁻¹ were used in all experiments. For the non-catalytic experiments 1.5 kg pure sand and for the catalytic experiments a catalyst–sand mixture of 1.5 kg (catalyst-to-sand mass ratio of 1:14) was used as the bed material. The reason for selecting a catalyst-to-sand weight ratio of 1:14 was to maintain the weight hourly space velocity WHSV [h⁻¹] at a value of around 1. The experimental run time (t_{run}) was kept at 60 min. in order to produce sufficient pyrolysis liquid for different types of analyses (*ca.* 50 g/run) and to allow a sufficiently high accuracy for the mass balance. This long experimental run time also allowed the pine particles to be completely devolatilized at the specified reaction temperature.

The products obtained from non-catalytic and catalytic fast pyrolysis are divided into liquid products (organics and water), carbonaceous solids (the sum of char, coke deposited on the catalyst, and the system deposits) and non-condensable gases (NCGs). ‘water’, as a pyrolysis product, refers to the water content (in wt.%) of the total liquid product determined by Karl Fischer titration. Hence the amount of ‘organics’ can mathematically be expressed as: organics = liquid products – water. System deposits can be defined as the carbonaceous matter other than char in the case of the non-catalytic experiments, and an average value of *ca.* 5 wt.% was obtained after having been checked a number of times.

The pyrolysis liquids were stabilized with a known amount of tetrahydrofuran (THF) to form a homogeneous (single-phase) liquid mixture and analysed for the H₂O content (Karl Fischer titration, KF) and their chemical composition (GC×GC/MS–FID). For the detailed characterization of pyrolysis liquids, a combination of GC×GC–FID and GC×GC–TOF–MS was used to get a high chromatographic resolution and on the other hand maximal agreement between both chromatograms. All analytical tools and the procedures that are used to characterize the pyrolysis liquids are detailed in the papers of Yildiz *et al.* [50,100] (Chapters 3 and 5 in this thesis) and Djokic *et al.* [180]. The micro carbon residue (MCR) values of pyrolysis liquids were taken from an Alcor MCRT-160, which automatically executes a factory programmed ASTM D4530 test program.

The elemental composition of char samples were determined by a Thermo Scientific Flash 2000 Organic Elemental Analyser. The ultimate analysis of pine wood was performed using Interscience Carlo Erba element analyser for C,H,N and O. Inductively coupled plasma (ICP) equipment from spectro and atomic emission spectrometer (AES) from Vista were used for the other elements [18].

The composition of non-condensable gases was determined off-line using a micro GC (Varian 490-GC) equipped with two TCD detectors and two analytical columns. The following gaseous compounds were measured: CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈ and H₂. The sum of C₂H₄, C₂H₆, C₃H₆ and C₃H₈ will be further referred to as C₂₊.

In this study, all the experiments and the analyses were performed at least in duplicate and averaged data are reported. The error bars in the figures represent standard deviations in absolute %'s. For the detailed information concerning the experimental unit, experimental procedures, yield calculations, and the collection and analyses of pyrolysis products, the reader is directed to our earlier publications [50,100].

6.2.3 Pyrolysis experiments

In this work, five types of pyrolysis experiments will be compared:

- i. A non-catalytic pyrolysis reference experiment (denoted as “NC”),
- ii. Non-catalytic pyrolysis after addition of biomass ash (denoted as “NC+ash”),
- iii. Catalytic pyrolysis with fresh catalyst as a reference experiment (denoted as “R0”),
- iv. Catalytic pyrolysis with fresh catalyst and added biomass ash (denoted as “R0+ash”), and finally
- v. Catalytic pyrolysis with catalysts obtained after eight successive reaction/regeneration cycles (denoted as “R8”).

The values obtained from five non-catalytic and three catalytic experiments with fresh catalyst were averaged to define the reference cases “NC” and “R0”, respectively. The mass balance closures for all experiments varied from 92 to 99 wt.%, while the scatter in measured data was always less than 5%. The standard deviations are shown in Fig. 6.2. Operating conditions for these experiments can be found elsewhere [50]. For all experiments, an identical experimental procedure was applied.

Bed materials obtained from the reference R0 experiments (char, sand and the spent catalyst mixture) were removed from the reactor after pyrolysis. Small amounts of char and spent catalyst/sand mixture were taken for their compositional analyses, and the rest was subjected to a two-step regeneration procedure (oxidative treatment to burn the coke and remove the carbon as CO₂) in a muffle furnace (based on the procedure proposed by Aho *et al.* [125]). Here, the oven temperature was increased from ambient to 250 °C (4.5 °C min⁻¹), and kept isothermal at 250 °C for 40 min. Then the temperature was raised to 600 °C (5 °C min⁻¹), and kept at 600 °C for 5 h. Finally the catalyst–sand mixture, regenerated in this way, was stored in the oven at 105 °C until the next experiment. The regenerated bed materials obtained from the reference R0 experiments were introduced back to the reactor and subsequent experiments were carried out (R1). This reaction/regeneration sequence was continued up to an 8th regeneration cycle which was denoted as “R8”. The experiments were started with three parallel batches, which were combined to two parallel batches after the sixth sequence to make up for the amount of material used for analyses and/or losses.

The ash that was initially present in the pine wood, and later in the char, was not removed actively during the successive regeneration steps but most likely remained in the bed material and thus may accumulate along the reaction/regeneration cycles. For a comparison, the same quantity of biomass originated ash that would have been accumulated in the bed material after eight regeneration cycles (*ca.* 3 g) was added to pure sand (NC+ash) as well as to fresh catalyst–sand blend (R0+ash). It is important to note that the predominant ash volatilisation mechanisms do not occur to a significant extent, neither at 600 °C (ashing temperature) nor at 500 °C (pyrolysis reaction temperature) [221]. Three identical experiments were performed for each case and the results were averaged.

6.3 Results and discussions

6.3.1 Effect of ash on the product yields

Fig. 6.2 shows the average product yield distribution on feedstock weight (as received) basis obtained from ash addition experiments compared to the reference experiments (NC, R0 and R8). The scatter in the product yields is less than 5% indicating sufficient reproducibility to draw conclusions with respect to the trends in the experiments.

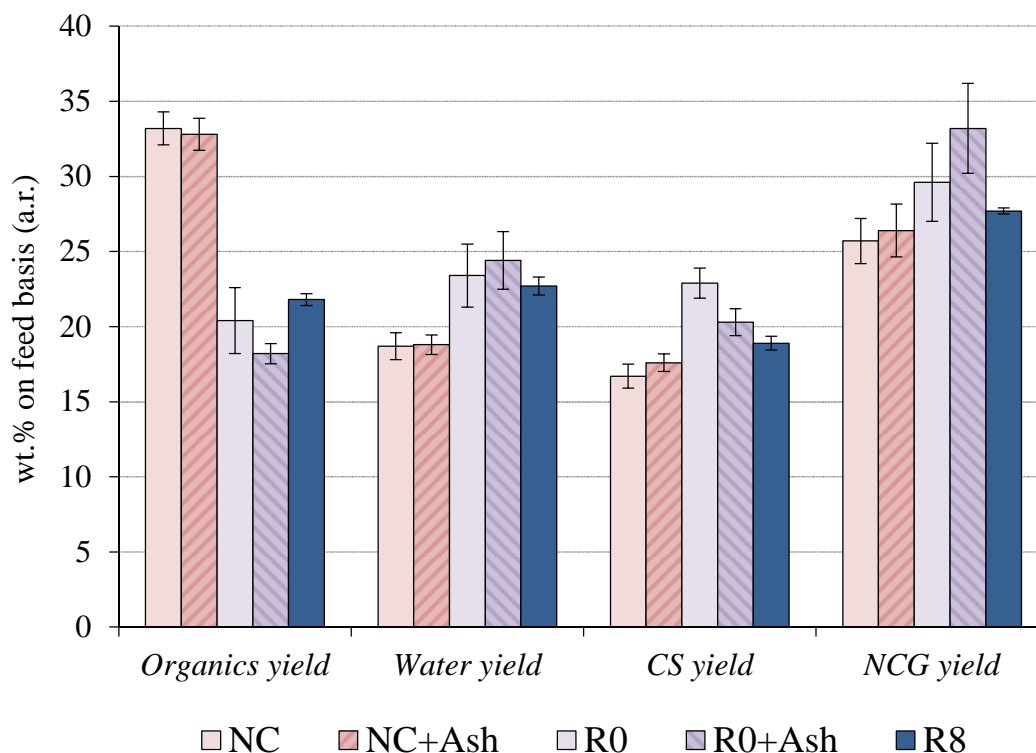


Fig. 6.2. Product yields obtained from ash addition experiments compared to those of the reference, non-catalytic (NC), the catalytic with fresh catalyst (R0), and the 8th cycle of catalyst regeneration (R8) experiments. Fast pyrolysis of pine wood at 500 °C.

The highest organics yield, and the lowest water, carbonaceous solids (CS) and NCG yields were obtained in the NC experiments. The addition of ash (NC+ash) had only a marginal effect in non-catalytic pyrolysis; the yield of organics decreased by 0.5 wt.%, and CS and NCG yields increased by almost 1 wt.%. Actually these values are within the experimental error, but their trends are in line with the literature [216,222]. Comparison of the catalytic experiment with fresh catalyst (R0) with the one having ash added (R0+ash), shows a larger difference in results. The presence of the added ash in catalytic fast pyrolysis induced an extra decrease in the yield of organics and carbonaceous solids by 2 wt.% for both. On the contrary, the water yield increased by 1 wt.% and the non-condensable gas yield increased by 4 wt.%, presumably due to the presence of ash (vapour cracking). The decrease in the yield of carbonaceous solids after ash addition (specifically the calculated coke, see Fig. 6.3 – R0 vs. R0+ash) points to a suppression of coke formation on the catalyst. Similarly, increases in both water and NCG yields and decreased yields of organics are indicative for additional cracking activity induced by the catalyst, the ash or a combination thereof. Because the ash content in R0+ash is much higher than in R0 (3 wt.% versus *ca.* 0.3 wt.% respectively, on feedstock basis), vapour cracking by ash components (Path 2 of Fig. 6.1), or in series by both the ash and the catalyst (Path 3a of Fig. 6.1) is likely to occur.

Comparing the yields obtained in R0+ash and R8, the differences are more pronounced. The organics yield of R8 is 4 wt.% higher, while the water, CS and NCG yields are 2, 1, and 6 wt.% lower, respectively. The presence of ash cannot be the only reason to account for these differences in product distribution, as the amount of ash present in pyrolysis is equal for both cases. However, the observed differences in the yields of pyrolysis products can be due to loss of activity of the catalyst itself, or another way of incorporation of the ash components in or on the catalyst. Although the loss of a part of the catalyst after eight reaction/regeneration cycles could be another cause; this has not been observed.

The individual yields of char and the system deposits were assumed to be *ca.* 12 wt.% and *ca.* 5 wt.%, respectively for all the experiments, due to the fact that each experiment has been carried out under identical process conditions; this has been verified a number of times. Besides, the residence time of pine wood particles in the bed ($t_{\text{run}}=60$ min) was always sufficiently long to allow for a complete devolatilization at the adjusted reaction temperature (500 °C). Hence, the differences in the yields of carbonaceous solids must indicate a change in the coke yield.

Fig. 6.3 shows the changes in calculated coke yield for three individual groups of catalytic experiments, *viz.* R0, R0+ash, and R8. After ash addition (R0+ash), the coke yield decreased by 3 wt.% compared to R0. An explanation could be that the minerals are interfering with the active sites inside the catalyst particles, effectively reducing the catalyst activity (Path 4 in Fig. 6.1). Another possible explanation could be that the metals contained in the ash favour the vapour cracking (Path 2 in Fig.1) and/or inhibit the formation of coke precursors.

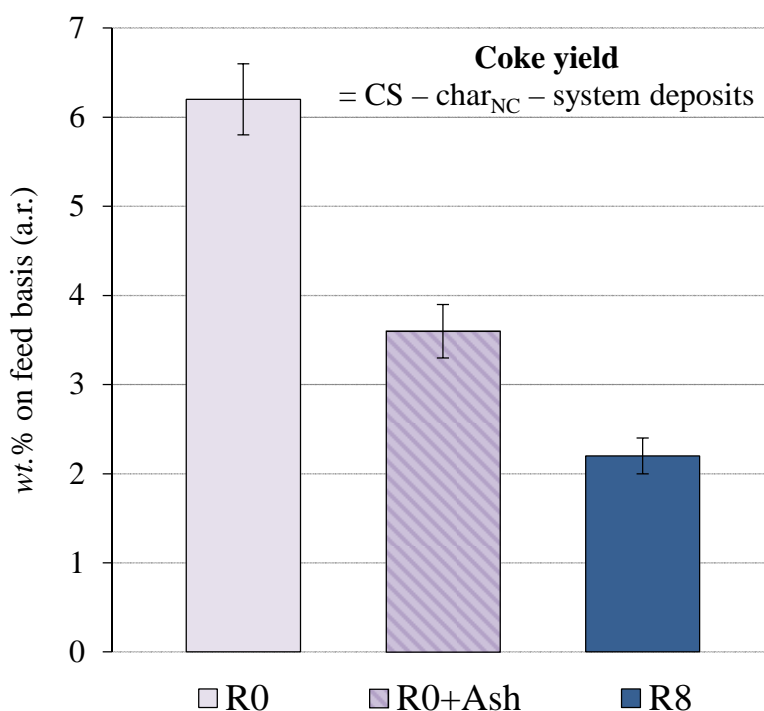


Fig. 6.3. Calculated coke yield obtained from ash-added catalytic experiments (R0+ash) compared to those of catalytic fast pyrolysis with fresh catalyst (R0), and the 8th cycle of catalyst regeneration experiments (R8). Fast pyrolysis of pine wood at 500 °C.

The coke yield of R8 was 4 wt.% and 1 wt.% lower than of R0 and R0+ash, respectively. When the results of R0+ash and R8 are compared, it is observed that although principally the same amount of ash is present in both cases, the coke yields are different. It should be noticed here that, during the eight reaction cycles changes occur on the catalyst/sand mixture. Obviously the apparent reduction in catalytic activity cannot be explained only by the presence of ash. Multiple reaction and catalyst regeneration cycles cause thermo-mechanical, chemical and/or physical changes in the catalyst structure, likely as a consequence of poisoning, fouling, dealumination, and attrition. The latter might even cause the catalyst content of the sand/catalyst mixture to be lowered. Hence, the lower coke yield found in R8 is largely due to an apparent reduction in catalyst activity as a consequence of the repeated regeneration of the catalyst/sand mixture.

6.3.2 Effect of ash on the yields of the individual non-condensable gas compounds

To further clarify the effect of ash on the cracking reactions, the yields of the individual non-condensable gas compounds are summarised in Table 6.3. Like in Fig. 6.2, the presence of ash seems to have a small effect in the case of the non-catalytic experiments. For both the non-catalytic (NC) and catalytic with fresh catalyst (R0) experiments, the presence of ash promoted the CH₄ and H₂ yields, while C₂₊ yields remained unaffected. The increase in CH₄ and H₂ yields may be attributed to vapour gasification reactions being enhanced by the minerals in ash. The reduced H₂ yield observed in R0, if compared to NC, suggests that hydrogen is consumed in the catalysed reactions (*e.g.* dehydration, hydrogenation of olefins or aromatics). Comparing the catalytic pyrolysis experiments R0 and R0+ash, ash seems to favour decarbonylation (CO production) and decarboxylation (CO₂ production) reactions, with a corresponding yield increase of 1 wt.% and 2 wt.%, respectively. As previously mentioned, the effect of ash on NCG production could be four-fold (Fig.1). The decrease in the CO/CO₂ ratio from 1.6 down to 1.4 shows that decarboxylation reactions are favoured in the presence of ash. The increase in CO_x (sum of CO and CO₂) yields is due to secondary vapour cracking reactions which is in line with the findings reported in the literature [216]. The yields of all non-condensable gas compounds in R8 were lower than the ones obtained from the R0+ash experiments, despite of a theoretically similar amount of ash present in both cases. On the other hand, the values obtained for NC+ash were quite close to the ones in R8 which indicates that (i) the catalyst has lost most of its apparent activity after 8 reaction/regeneration cycles and/or is partially lost, thereby yielding pyrolysis product distributions more akin to the non-catalytic case and (ii) some differences with respect to NC can be attributed to ash accumulation or some combined catalyst-ash effect. Both the yields of CO and CO₂ decreased by 2 wt.% in R8, if compared to R0+ash. The higher CO/CO₂ ratio for R0 showed that the type of deoxygenation via gaseous species is different than the experiments wherein the ash is involved (R0+ash and R8). This suggests that the change in the activity of the catalyst is not only related to the presence of ash but also to physical and chemical changes in the structure or in the composition of the catalyst/sand mixture.

Table 6.3. Average non-condensable gas compound yields obtained from ash addition experiments. Values are compared to the reference, the non-catalytic (NC), the catalytic fast pyrolysis with fresh catalyst (R0) experiments, and the 8th cycle of catalyst regeneration experiments (R8). Product yields and standard deviations are represented in *wt.%* on feed basis (a.r.) and absolute %'s, respectively. Fast pyrolysis of pine wood at 500 °C.

	<i>NC</i>	<i>NC+ash</i>	<i>R0</i>	<i>R0+ash</i>	<i>R8</i>
CO	13.0 ± 0.8	13.4 ± 1.1	16.2 ± 1.7	17.3 ± 1.4	14.9 ± 0.3
CO ₂	10.0 ± 0.7	9.9 ± 0.5	10.1 ± 1.1	12.1 ± 1.2	9.7 ± 0.5
CH ₄	1.6 ± 0.1	2.1 ± 0.2	1.3 ± 0.2	1.7 ± 0.0	1.6 ± 0.1
C ₂₊	0.38 ± 0.02	0.41 ± 0.04	0.87 ± 0.11	0.86 ± 0.18	0.54 ± 0.06
H ₂	0.10 ± 0.01	0.12 ± 0.01	0.05 ± 0.00	0.08 ± 0.00	0.07 ± 0.00
CO _x ^a	22.9 ± 1.5	23.2 ± 0.5	26.3 ± 2.7	29.4 ± 2.6	24.6 ± 0.2
CO/CO ₂ ^b	1.30 ± 0.03	1.35 ± 0.04	1.61 ± 0.09	1.43 ± 0.03	1.54 ± 0.10

^a CO_x yield is the sum of CO and CO₂ (in *wt.%*)

^b CO/CO₂ ratio is dimensionless (*wt./wt.*)

6.3.3 Effect of ash on the composition of pyrolysis liquids

Fig. 6.4 shows the yields of compounds detected by GC×GC/MS–FID analysis. They are being classified according to their functional group, and ordered by the type of experiments. Included are sugars, aldehydes, acids, furans, ketones, phenols, aromatics and others (unclassified oxygenates such as 1-hydroxy-2-propanone). Table 6.4 shows details of the most prevalent individual compounds detected via GC×GC/TOF–MS analysis and quantified by GC×GC/MS–FID. For the quantification procedure, the reader is referred to the paper of Djokic *et al.* [180]. It should be taken into account that the yields shown in Fig. 6.4 and Table 6.4 were normalized and expressed on an as-received (a.r.) feed basis.

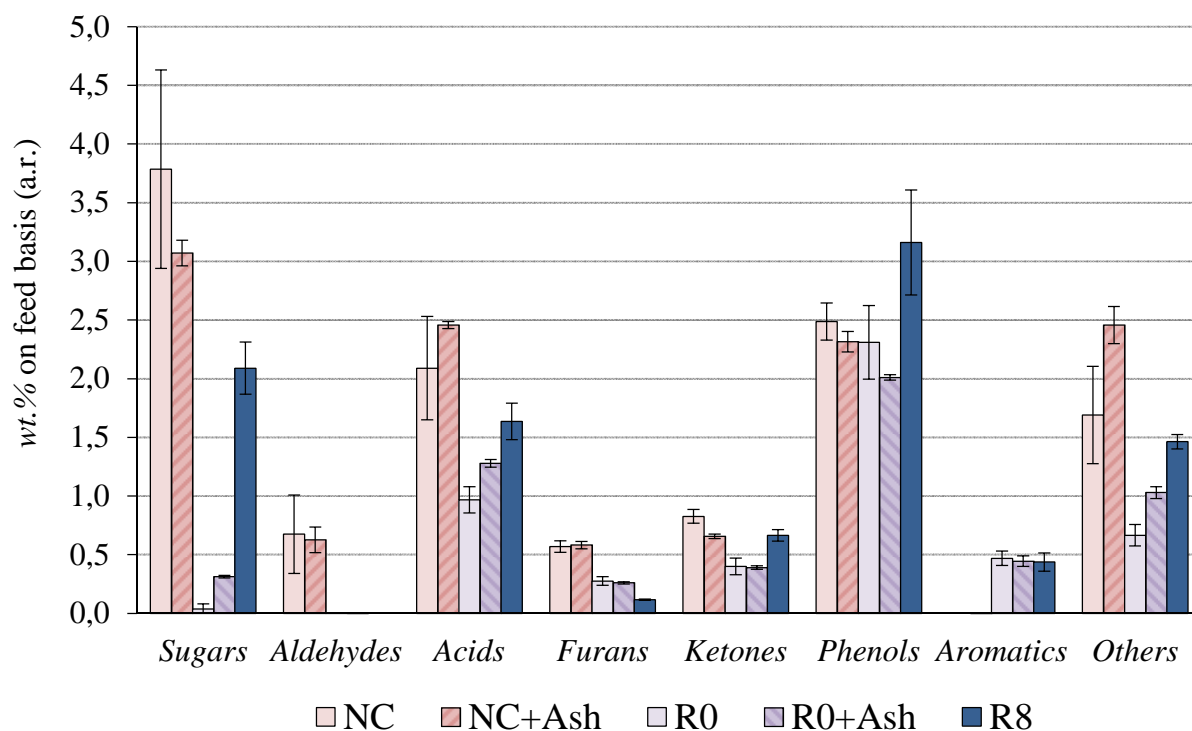


Fig. 6.4. Yields of functional groups in pyrolysis liquid (GC×GC/MS-FID detectable only) are shown for ash addition experiments, compared to the reference, non-catalytic (NC), the catalytic fast pyrolysis with fresh catalyst (R0), and the 8th cycle of catalyst regeneration experiments (R8). Fast pyrolysis of pine wood at 500 °C.

As shown by Fig. 6.4 and Table 6.4, the chemical composition of the detectable part of the pyrolysis liquid is significantly influenced by the presence of the catalyst. Besides, effects can be observed caused by the presence of the ash. Comparing NC and R0, the most important observations related to the presence of the catalyst were the complete suppression of the sugars and aldehydes as well as a significant decrease in acids, furans, ketones, and compounds classified as “others” (*i.e.* unclassified oxygenates). The quantity of the aromatics was increased as well.

Table 6.4. Yields of the most prevalent compounds in pyrolysis liquid (GC×GC/MS–FID detectable only) in case of ash addition experiments, compared to the reference, non-catalytic (NC), catalytic fast pyrolysis with fresh catalyst (R0) experiments, and the 8th cycle of catalyst regeneration experiments (R8) of pine wood at 500 °C (wt.% averages on feed basis (a.r.)).

	NC	NC+ash	R0	R0+ash	R8
<i>Sugars (3 compounds)</i>	3.79	3.07	0.04	0.31	2.09
Levoglucosan	3.22	2.58	0.00	0.29	1.84
<i>Aldehydes (2 compounds)</i>	0.67	0.63	0.00	0.00	0.00
Hydroxyacetaldehyde	0.67	0.60	0.00	0.00	0.00
<i>Acids (9 compounds)</i>	2.09	2.46	0.97	1.28	1.64
Acetic acid	1.50	1.99	0.57	0.94	1.16
Propanoic acid	0.29	0.16	0.07	0.09	0.13
<i>Furans (12 compounds)</i>	0.57	0.58	0.28	0.26	0.12
Furfural	0.22	0.15	0.06	0.08	0.02
<i>Ketones (9 compounds)</i>	0.83	0.66	0.40	0.39	0.66
2-cyclopenten-1-one	0.16	0.16	0.14	0.17	0.34
<i>Phenols (24 compounds)</i>	2.49	2.31	2.31	2.01	3.16
1,2-benzenediol	0.51	0.46	0.37	0.32	0.50
4-methyl-1,2-benzenediol	0.61	0.59	0.43	0.36	0.69
4-ethylcatechol	0.29	0.26	0.21	0.17	0.34
2,4-dimethyl-phenol	0.19	0.14	0.21	0.16	0.21
4-methyl-phenol	0.11	0.11	0.28	0.24	0.27
2-methyl-phenol	0.10	0.10	0.17	0.16	0.18
Phenol	0.08	0.08	0.28	0.24	0.24
<i>Aromatics (19 compounds)</i>	0.00	0.00	0.47	0.45	0.44
Xylene (m, -p)	0.00	0.00	0.03	0.01	0.01
1-methyl naphthalene	0.00	0.00	0.24	0.18	0.09
Methyl-1H-indenes	0.00	0.00	0.06	0.07	0.06
Indene	0.00	0.00	0.03	0.03	0.02
Indane	0.00	0.00	0.01	0.01	0.01
<i>Others (21 compounds)</i>	1.69	2.46	0.67	1.03	1.46
1-hydroxy-2-propanone	1.08	1.45	0.20	0.47	0.80

In fast pyrolysis, the mineral salts/ash present in biomass lowers the activation energy of reactions leading to the direct formation of the lower molecular weight decomposition species of cellulose, such as; glycolaldehyde (hydroxyacetaldehyde), formic acid, acetol and gas compounds. The reason for decreased levoglucosan yields is that the preferential activation of these reactions reduces the amount of cellulose available for the reactions that produce levoglucosan [212,223,224]. In our study, the presence of ash (NC vs. NC+ash) revealed clear changes in the yields of some chemical species such as a decrease in the levoglucosan yield and increased yields of acetic acid and 1-hydroxy-2-propanone (acetol) (Table 6.4), which are in line with the literature. The presence of potassium and calcium in the form of CaCl_2 has a decreasing effect on the levoglucosan yield [212] while magnesium has the opposite effect [213]. Moreover, alkaline earth metal chlorides (MgCl_2 , CaCl_2) were reported to increase the char yield in cellulose pyrolysis at 400 °C while decreasing the yield of levoglucosan [225]. This would impact the observed coke yield, since it is assumed here that char yield is always the same as for non-catalytic (see also Section 6.3.1). In order to achieve higher levoglucosan yields, biomass would need to be demineralized down to certain concentrations [212]. By the removal of alkali and alkaline earth metals, increased yields of lignin-derived oligomers in the pyrolysis liquid were observed as well [217]. The decrease in phenols both in non-catalytic and catalytic experiments with and without ash (Table 6.4) was in line with this observation.

In CFP of biomass with acidic zeolites, the catalyst is known to promote cracking reactions leading to production of highly deoxygenated and hydrocarbon-rich compounds via acid catalysed dehydration, decarbonylation and decarboxylation reactions [44,109]. In the case of experiments with fresh catalyst with and without ash addition (R0 and R0+ash), increases in yields of sugars, acids and other oxygenates were observed after the addition of ash. Especially the increase in sugar yields, which was not the expected scenario in the presence of the ash (as explained before), revealed that the catalytic activity was changed by the addition of the ash. This can be explained by the deposition or adsorption of ash derived chemical species (*e.g.* AAEMs) on the catalyst surface, thereby blocking either the active sites or the pores inside the catalyst and reducing its activity. On the other hand, the production of aromatics and ketones was not affected by the presence of ash. After several regeneration cycles the situation is again different. For R8, compared to R0+ash, the yields of sugars increase (from 0.3 wt.% to 2.1 wt.%), together with acids (acetic acid from 0.9 wt.% to 1.2 wt.%), ketones (doubled 2-cyclopenten-1-one yield from 0.2 wt.% to 0.3 wt.%), phenols (increases in catechol, 4-methyl-catechol and 4-ethyl-catechol) and other oxygenates (increase in for example 1-hydroxy-2-propanone from 0.5 wt.% to 0.8 wt.%). Conversion of aldehydes in both cases, and a similar yield in aromatics revealed that the catalyst still had a certain activity, even after eight cycles. Unfortunately the significant difference regarding the production of detectable phenols cannot be explained very well in this stage of research. R8 shows a level higher than all other cases. In our earlier paper concerning the effect of successive catalysts regeneration [50], the rising level of phenols was observed particularly during the last three cycles.

While looking at the results shown in Fig. 6.4, it should be kept in mind that the compound conversions may not be limited only by the reduction of acid sites in the catalyst's interior, but also by the presence of sufficient reaction precursors in the vapour phase, the catalyst accessibility, and/or changes in the ratio of sand to catalyst due to catalyst attrition or selective removal (relatively large difference in density and particle size). Overall, it can be concluded that the deactivation of the catalyst is not only related to the presence of ash but also caused largely by the thermo-mechanical, chemical or physical changes (*e.g.* poisoning, fouling, attrition, and amount) occurring during the eight reaction/regeneration cycles.

6.3.4 Effect of biomass ash on the elemental distribution over various pyrolysis products

Table 6.5 shows the elemental distribution over various pyrolysis products (organics, water, char, coke, and NCGs) obtained from the ash addition experiments, compared to the reference experiments (NC, R0 and R8). The presence of ash in case in non-catalytic pyrolysis had almost no effect regarding the elemental distribution over the various pyrolysis products. On the other hand, the addition of ash in R0+ash caused some slight changes in the elemental distribution when compared to the catalytic experiments with fresh catalyst only (R0). The carbon content of the organic fraction of pyrolysis liquid slightly decreased by 2 % while it increased by the same amount in NCGs. That supports the hypothesis that ash minerals are able to crack the larger molecules of the primary vapours (Path 2 in Fig.1). Char and coke yields were not affected. For hydrogen and oxygen, the changes are clearer, as they decreased by 4 % and 7 %, respectively. The hydrogen and oxygen yields for the aqueous phase (associated with the increase in the water yield) increased by 3 % for both. Hydrogen and oxygen yields in the non-condensable gases increased by 2 % and 3 %, respectively. These findings revealed that, in line with the above shown results, the presence of ash increased the water and NCG production (particularly CO₂).

When the results obtained in the R8 experiment were compared to R0+ash, significantly more carbon, hydrogen and oxygen from the feed ended up in the organics; they were increased by 5 %, 8 % and 12 %, respectively. These results show that the redistribution of C, H and O from the feedstock towards the pyrolysis product fractions in the R8 experiments was more similar to those of non-catalytic (NC) experiments which can be interpreted as a sign of selective catalyst deactivation and/or loss. The decreased elemental contents in coke and NCGs are in line with that suggestion; see also Fig. 6.3 and Table 6.3.

Table 6.5. Elemental distribution over various pyrolysis products obtained in ash addition experiments. Values are compared to the reference, the non-catalytic (NC), the catalytic fast pyrolysis with fresh catalyst (R0) experiments, and the 8th cycle of catalyst regeneration experiments (R8). Values shown are mass fractions in %, relative to the carbon, hydrogen, oxygen present in the biomass feed. Fast pyrolysis of pine wood at 500 °C.

	<i>NC</i>	<i>NC+ash</i>	<i>R0</i>	<i>R0+ash</i>	<i>R8</i>
<i>Carbon</i>					
Organics ^a	59.4	60.2	51.5	49.9	55.3
Water ^b	–	–	–	–	–
Char	19.9	19.4	19.7	19.7	19.6
Coke ^c	5.1	5.1	11.2	11.2	7.5
NCG ^d	15.6	15.3	17.6	19.2	17.6
<i>Hydrogen</i>					
Organics ^a	45.8	45.0	33.2	28.9	36.4
Water ^b	35.2	35.4	43.1	45.9	42.7
Char	6.7	6.5	6.4	6.4	6.3
Coke ^c	4.5	4.5	9.9	9.9	6.7
NCG ^d	7.8	8.6	7.4	8.9	8.0
<i>Oxygen</i>					
Organics ^a	34.2	33.4	17.8	11.2	23.5
Water ^b	35.8	35.5	43.2	46.1	42.9
Char ^e	1.9	3.1	2.9	4.0	1.2
Coke ^c	4.3	4.3	9.4	9.4	6.3
NCG ^d	23.8	22.6	25.6	28.4	25.1

^a Calculated by difference.

^b Based on the results of Karl Fischer analyses.

^c Coke refers to coke on catalyst. The elemental composition of coke was obtained (the given values were averaged) from Williams and Horne [195].

^d Derived from micro-GC analyses.

^e Oxygen in char was calculated by difference.

When the aim is to produce pyrolysis liquids that are compatible with petroleum feedstock, the final product is usually evaluated by its O/C and H/C ratio. A low O/C and a high H/C ratio indicate a better quality liquid [73]. In general, oxygen rich aromatic feedstock are characterized by high micro carbon residues (MCR), low H/C ratios and are highly polar, and they are forming considerable amounts of coke (2-8 wt.%) during cracking [226]. Moreover, the coking tendency of the pyrolysis liquid increases with increasing MCR values which is an indication of heavy oxygenated components. In biomass fast pyrolysis, the presence of a catalyst reduces the micro-carbon residue (MCR) of the pyrolysis liquid [64,227]. Table 6.6 shows the MCR values and H/C ratios of the liquid products (organics + water). In non-catalytic fast pyrolysis of pine, the addition of ash reduced the MCR value from 8.3 wt.% to 7.1 wt.%. In the literature, the MCR of non-catalytic pyrolysis liquid is reported to be in the range from 16 to 20 wt.% [64]. The lower MCR values found in this study may be the result of significant cracking of the vapours as a consequence of relatively

long hot vapour residence times. In case of catalytic fast pyrolysis with fresh catalyst, an opposite effect of ash addition was observed; the MCR value increased from 2.5 wt.% to 3.7 wt.%. This could be caused by deactivation of the catalyst due to adsorption/clogging with biomass-derived minerals – which would increase the MCR. And consequently, the decreasing effect of ash on the MCR (through more intense cracking) is more than negated by the reduction of catalyst activity due to the mineral contamination of the catalyst (which increases the MCR). The MCR value of R8 was 3.4 wt.% and slightly smaller than that of R0+ash. Compared to that of non-catalytic experiments, the H/C ratio of the liquid product increased in case of the catalytic pyrolysis. However, the addition of ash (both in non-catalytic and catalytic cases) seemed to have almost no effect on the H/C ratio of the liquid product.

Table 6.6. MCR values and H/C ratios of the liquid products (organics + water) obtained from ash addition experiments, compared to the reference, non-catalytic (NC), the fresh catalyst (R0), and the 8th cycle of catalyst regeneration experiments. Fast pyrolysis of pine wood at 500 °C.

	<i>NC</i>	<i>NC+ash</i>	<i>R0</i>	<i>R0+ash</i>	<i>R8</i>
MCR (wt.%)	8.25	7.14	2.50	3.67	3.42
H/C	1.36	1.33	1.48	1.50	1.43

6.4 Conclusions

Accumulated ash may negatively affect the efficiency of the catalyst by its influence on the composition of the primary pyrolysis vapours to be reformed by the catalyst (pathway 4 in Fig. 6.1). Ash concentrations as low as *ca.* 3 wt.% relative to the amount of pine wood fed, and *ca.* 0.002 wt.% relative to the amount of bed material, were found sufficient to have a direct effect on the yield and composition of the catalytic fast pyrolysis products. With the presence of ash in catalytic pyrolysis, the yield of organics decreased by 2 wt.% while increases in the water (1 wt.%) and non-condensable gases (4 wt.%) were observed. Moreover, sugars and acids increased and phenols decreased. Although the effects are different in their details, the impact of accumulated ash in catalytic fast pyrolysis is comparable with that of selective catalyst losses and/or catalyst deactivation. The latter could then be well enhanced by the accumulated ash. To overcome the drawbacks of biomass ash in catalytic fast pyrolysis, the char (which contains a vast majority of the biomass ash) has to be physically removed from the catalyst before the regeneration step. The biomass feedstock used in this study (pine wood) is a low-ash feedstock. With the use of high-ash containing feedstock, and the larger number of reaction/regeneration cycles desired in future large scale installations, the effect of ash will be even more dramatic. Future research should reveal whether the observed trends will persist after many more reaction/regeneration cycles, and how long it takes for the catalyst to completely deactivate. Strategies to reduce the minerals (*e.g.* biomass leaching, char removal prior to the regeneration step) burden in the catalytic fast pyrolysis process could extend the lifetime of the catalyst.

Chapter 7

Challenges in the design and operation of processes for catalytic fast pyrolysis of biomass

In this chapter, an extensive discussion regarding the technical and operational barriers for the implementation of catalytic fast pyrolysis technology is provided while focusing on the most suitable process modes and parameters, efficient and economical use of the primary and secondary products, and the heat integration of the process. Some process alternatives for an efficient CFP operation are suggested as well.

7.1 Introduction

One of the reasons that food/feed industries, refinery companies, and catalyst companies show a distinct interest in thermochemical biomass conversion processes these days, is the society driven demand for second generation biofuels, bio-based chemicals, and/or chemical intermediates (for more detailed information see Chapter 1 in this thesis). Fast pyrolysis is a fairly simple biomass liquefaction technique that offers significant logistic advantages in enabling shipping to central sites (*e.g.* refineries, chemical plants, power stations) for large scale conversion to final products. Being non-selective, fast pyrolysis accepts a wide variety of lignocellulosic feedstock materials such as forestry, agricultural or plantation residues, and industrial waste streams from *e.g.* food/feed, bio-ethanol, or bio-diesel production.

While the distributed availability and low energy density of biomass is a problem in storage and transportation, a possible solution is the local densification of biomass via liquefaction (by fast pyrolysis), followed by a centralised utilization at any desirable place, time, and scale. Apart from nearby applications such as combustion in boilers, turbines, or engines for the production of heat and electricity (CHP), the upgrading of bio-oil in a dedicated biorefinery seems attractive as well. Centralised biorefineries may include crude bio-oil conversion and upgrading technologies such as gasification and synthesis (*e.g.* Fischer-Tropsch process), fluid catalytic cracking, hydroprocessing (hydrocracking and hydrotreatment), steam reforming, *etc.* [77]. However, the construction of a new bio-oil based biorefinery is a riskful and expensive affair and venture capitalists are currently not willing to invest in its development due to high economic risks.

In any scenario for the production of upgraded bio-oils, the goal is usually to produce either high yields of transportation fuel compounds (*e.g.* aromatics, olefins) and specialty chemicals (*e.g.* phenolics), or just a drop-in refinery feedstock to be blended in with the products from existing petroleum refineries. Moreover, co-processing of a mildly upgraded bio-oil without any major modification in the existing petroleum infrastructure would limit the costs and aforementioned investment risks significantly. When fast pyrolysis of biomass is carried out in the presence of suitable heterogeneous catalysts (*i.e.* catalytic fast pyrolysis: CFP), the quality of the liquid product can be improved for an increased compatibility with crude oil based refinery feedstock, and thus further upgrading processes may be avoided or minimized. In CFP of biomass, the chemical composition of crude bio-oil can be shifted from its typical polar nature more towards petroleum-like products [86,228] in an economical single-step process. The process yields a liquid product composed of two phases, *viz.* an aqueous phase (rich in water and acids) and a heavy phase rich in (partially) deoxygenated organic compounds (*i.e.* CFP-oil). In principal, the latter can be used to co-feed a fluid catalytic cracking unit (FCC) in existing petroleum oil refineries [63]. That would enable the production of drop-in hydrocarbon fuels without building a separate bio-oil refinery. Hence, in a CFP process, consideration should be given to the production of liquid intermediates instead of finished fuels. The objective is to improve the physical and chemical properties of the pyrolysis liquids (*e.g.* removal of oxygen, elimination of acidic compounds) in a way that they become compatible with the regular refinery unit feedstock. It should be noticed however that the development of CFP is in its infancy in comparison with other thermo-chemical

technologies (*e.g.* gasification), and the required product specifications are still fairly undefined.

Together with the quality and the market value of the products, the efficiency and the scale of operation also determines the feasibility of a CFP process. When the availability of the selected type of biomass feedstock is geographically limited, CFP may be better suited for small scale distributed plants. On the other hand, larger scale centralised CFP plants can also be realized in case of a sufficient supply of the biomass feedstock. In the economic standpoint, such installations should be self-sustaining in terms of their internal heat requirements and also have high energy efficiency.

Most of the literature studies concerning CFP of biomass deal with the catalyst screening in small scale laboratory systems, however there is a big gap and lack of input regarding the process operation and design. In recent years, various project developers (see Chapter 2 in this thesis) have tried to push catalytic fast pyrolysis to the pilot scale, or even to a commercial scale, but with varying degrees of success. This chapter reviews and discusses the way of implementing CFP technology in a process oriented way while focusing on the most suitable process modes and parameters, the heat integration, and some possible process alternatives. The final goal is to come up with some recommendations and suggestions on how to realize this technique at a commercial/industrial scale.

7.2 The purpose of catalysis in fast pyrolysis of biomass

The general intention of applying catalyst materials in chemical processes is to lower the reaction temperature and/or to improve the selectivity to the desired products. It has been recognized already in the early days of fast pyrolysis R&D [38] that the application of catalysis could be of major importance in controlling the quality and the chemical composition of the liquid product. Catalysis could be applied at a number of different positions in a fast pyrolysis process; they could be impregnated in the biomass feed, mixed with the biomass in the fast pyrolysis reactor (*in situ* operation), built in the process after the fast pyrolysis reactor for the reforming of primary pyrolysis vapours (*ex situ* operation), or be used to modify the condensed liquids (*e.g.* hydrodeoxygenation). It should be noticed that these options could be applied separately or in various combinations. Fig. 7.1 illustrates the possible catalyst insertion points in a fast pyrolysis process.

Without any catalyst involvement, the bio-oil derived from fast pyrolysis of biomass (*i.e.* crude bio-oil) is a mixture of hundreds of different, highly oxygenated chemical compounds with molecular weights ranging from 18 g/mol (*i.e.* water) up to 5000 g/mol or more (*e.g.* oligomers) [12]. This chemical mixture also has some unfavourable properties such as a high oxygen content, a high acidity, an insufficient chemical stability and a low heating value [30]. Besides, none of the individual compounds in the crude bio-oil are present in quantities above a few weight percent.

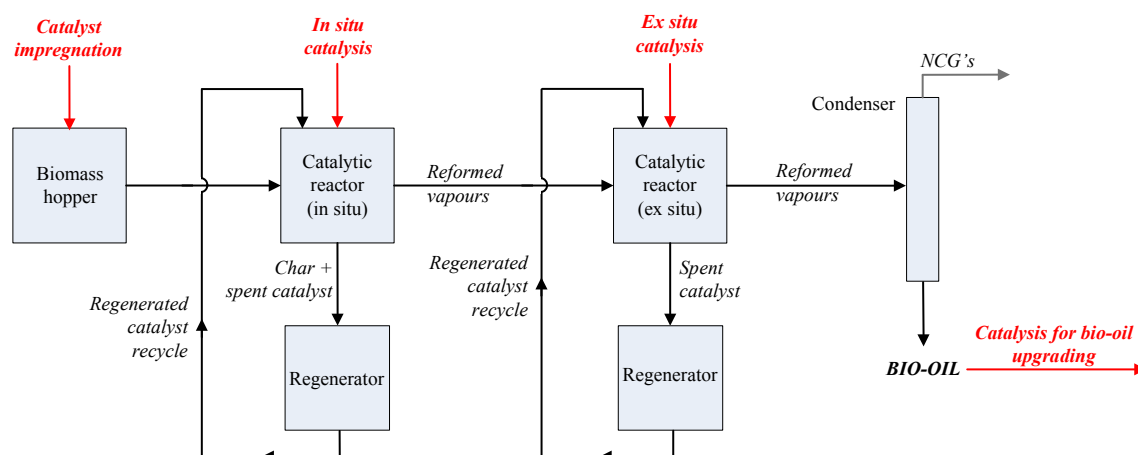


Fig. 7.1. Options for the addition of catalyst materials in a fast pyrolysis process.

The presence of oxygen is commonly believed to be the origin of the problems in pyrolysis oils. However, while realizing that second generation bio-fuels may contain significant amounts of oxygen (like in ethanol or methanol), it is postulated here that not the oxygen itself is a problem, but the way in which the oxygen is present in the bio-oil. If the quality of the oils should be steered, whether or not in combination with a certain degree of oxygen removal, that would include a selective transformation of the oxygen functionalities into ‘desired’ or acceptable ones like alcohols and ethers. Undesired chemical compounds are those with very reactive functional groups, *e.g.* carboxylic acids, aldehydes, ketones. A key issue to learn, by proper oil analysis, is the nature and the quantity of the oxygen containing groups present in the oil, and how their presence can be changed selectively. Certain combinations of different oxygen functionalities like acids/alcohols or alcohols/aldehydes are also undesired as they can easily lead to polymerization reactions during handling and storage of the bio-oil. All this leads to the conclusion that steering of the oxygen functionalities should be a main concern in upgrading of pyrolysis oils, next to a (partial) reduction of the oxygen content (preferably by CO₂ rejection; see Chapter 2 in this thesis). A general observed trend in the literature on catalytic fast pyrolysis is that the product and energy yields are very low for high de-oxygenation levels [63]. Depending on the precise end use of the product, one should find ways to control the catalytic effect and search for an optimal impact of the catalysis.

Catalysis can significantly alter the bio-oil composition by promoting deoxygenation, cracking, and reforming (re-arranging structures of hydrocarbon molecules) reactions. The intention here is to convert the primary products of thermal decomposition (poly-sugar and lignin fragments) preferably into *iso*-alkanes and (*mono*-) aromatics. There are various performance criteria for the catalysis in CFP (see Tables A.4.3a and A.4.3b in the Supporting Information). One of them is to keep as much chemical energy in the desired product as possible (compared to the energy input by the original biomass feedstock); this can be achieved largely by limiting the formation of coke on catalyst (carbon loss), water (hydrogen loss), and water soluble organics. More importantly, the efficiency of a catalyst can be evaluated by its ability to remove oxygen from the CFP-oil and to produce either higher-

octane-number gasoline components and/or intermediates for the production of bio-based chemicals.

7.3 The ideas behind catalytic fast pyrolysis

The aim of a commercial CFP process should be to convert the biomass feedstock efficiently to a high-quality liquid (CFP-oil) in high quantities, which could be realized by:

- the stabilization of the liquid product by controlling the molecular size distribution and steering the oxygen functionalities,
- the (partial) removal of oxygen from the liquid product preferably by CO₂ instead of H₂O and CO,
- the minimization of coke formation on the catalyst,
- the maximization of the energy yield,
- the production of (*iso*-) alkanes and aromatics,
- accepting stable oxygenates like alcohols, ethers and phenols.

In CFP of biomass, the possible options are to produce:

- a. a feedstock for the FCC units in the existing crude oil refineries, in which case the CFP-oil should be miscible with vacuum gas oil (VGO) or light cycle oil (LCO),
- b. a bio-fuel for direct use in large engines (trains and ships, stationary engines and turbines in co-generation units),
- c. blendable components for transportation fuels (gasoline or diesel), which would require the isolation of specific compounds (*e.g.* aliphatic and/or aromatic hydrocarbons) from the CFP-oil.

Other important targets should be the limitation of the energy demand of the process, the amounts of by-products, and the consumption of the fresh catalyst. The latter requires an effective regeneration of the spent catalyst. Eventually, five main factors influence the effectiveness of a CFP process:

- the type and the properties of the biomass feedstock,
- the type of the catalyst used,
- the process parameters (*i.e.* temperature, heating rate, catalyst-to-feed ratio, vapour residence time, *etc.*),
- the operation mode (*i.e.* in- or ex situ),
- and the choice of the reactor technology.

The success of the process, in relation to the target product properties, is strictly related to the precise optimization of these factors.

7.3.1 Technical factors influencing the effectiveness of a CFP process

(This section includes the summary of the highlights of what was discussed in Chapter 2 in this thesis, where more detailed information regarding the contents of this section can be found.)

7.3.1.1 Biomass feedstock

Although a wide variety of lignocellulosic feedstock materials can be utilized, high lignin and low ash containing biomass feedstock should be preferred in CFP of biomass. Compared to cellulose and hemicellulose, lignin has a lower oxygen content. The presence of aromatic moieties in lignin makes it suitable for the production of phenolic intermediates which then can be converted to aliphatic and aromatic hydrocarbons with a suitable catalyst (see Fig. 2.5 in Chapter 2 in this thesis). On the other hand, high ash containing biomass feedstock (*i.e.* agricultural residues, non-woody biomass, *etc.*) are not desirable for CFP due to the catalytic effect of ash under pyrolysis conditions (*i.e.* vapour cracking) [29], due to the deactivation of the catalyst by the presence of ash, and due to an increase in undesirable compounds (*i.e.* acids) [81] (see Chapter 6 in this thesis). Compared to other types of biomass feedstock, woody biomass meets the above mentioned specifications [80] and may enable the production of high yields of CFP-oil with higher heating value. Literature studies (see Chapter 2 in this thesis) also show that woody biomass has been used in most of these studies due to the fact that it is relatively clean, easy to process (*e.g.* handling and feeding), and well characterized (especially for some specific wood types, such as pine and beech). Besides, it has a vast availability on the international market.

Ideally, biomass feedstock materials with a moisture content below 10 wt.% are preferred in fast pyrolysis processes [29] (see Chapter 2 in this thesis). Higher moisture content in the biomass feedstock will cause excessive water content in the bio-oil, thereby reducing its heating value. Also, the higher the moisture content, the more energy is required to heat the feedstock up to the pyrolysis temperature (as more latent heat is consumed). In this case, a biomass pretreatment unit including a drying step should be included in the process. For the biomass feedstock having ash contents higher than that of woody biomass (*i.e.* *ca.* 0.5 wt.% [80]), a leaching step before the drying step could be considered (see Fig. 7.5a and Fig. 7.6) [229]. Leaching refers to washing the biomass feedstock with an acidic solution and/or water for (at least partial) demineralization.

7.3.1.2 Catalyst

One of the most important challenges for CFP of biomass is to design efficient and economical catalysts. The extensive research into catalyst design and screening has been detailed in some recent literature reviews [63,230,231]. The ideal CFP catalyst should be cheap, strong, stable, resistant to coke formation, regenerable, and effective in terms of its activity and selectivity. As expected however, compared to the conventional fast pyrolysis processes, the use of heterogeneous catalysts in CFP of biomass results in additional costs and processing difficulties (*e.g.* excessive deactivation of the catalyst). It is estimated that the cost of a CFP process might be around twice that of a pyrolysis-only process (in terms of dollar per joule of energy produced from the oil) although this could decrease with an increased scale of production [40,232].

7.3.1.3 Process parameters

The process parameters that should be taken into account in CFP of biomass are: the temperature, the residence time and the heating rate of the biomass, catalyst-to-biomass ratio, and the vapour residence time.

The reaction temperature is one of the main, if not the major, critical process parameters in CFP; it affects the relative rate of the catalysed vapour phase reactions [40]. In *in situ* catalytic fast pyrolysis of biomass, where the catalyst and the biomass are mixed together in a heated reactor zone (see section 7.3.1.5), the temperature of the catalyst is same as (and thus limited by) the actual biomass fast pyrolysis temperature (*ca.* 500 °C). However, in the *ex situ* mode, where the biomass fast pyrolysis and the catalytic reactors are heated separately, the temperature of the catalytic reactor can be adjusted to lower or higher temperatures than that of the fast pyrolysis reactor. This could be beneficial regarding the outcome of the process so that the temperature of the catalytic (*ex situ*) reactor could be set precisely based on the optimal performance of the applied catalyst with respect to product yield and quality.

The heating rate of a biomass particle is closely related to its particle size. In transported bed reactors operated either catalytically or non-catalytically, biomass particles smaller than 2 to 3 mm are necessary to achieve high heating rates and complete devolatilization within a short retention time [29]. In these type of reactors, the external medium-to-solid heat transfer rates should also be sufficiently high ($>500 \text{ W/m}^2\text{K}$ [30]). This is achieved when the biomass particles are submerged quickly in a bed of hot, fine particles of inert solid material (*e.g.* sand) [233].

In a continuously operating CFP reactor, the mass ratio of catalyst-to-biomass should be optimised precisely to ensure a sufficient contact area for the adsorption of the primary pyrolysis vapours on the catalyst surface (active sites). When the amount of the catalyst (and thus the active surface area) is not sufficient, some of the primary pyrolysis vapours could leave the reactor without being reformed, yielding a mixture of catalyzed and non-catalyzed liquid product. Adversely, in the case of the presence of excess catalyst in the reactor, the economics of the process could be affected negatively due to the dispensable attrition of the catalyst in continuous systems where reaction-regeneration cycles are involved. Moreover, the

overcracking of the vapours resulting in the formation of undesired non-condensable gas compounds is possible as well.

In a regular fast pyrolysis process, short vapour residence times (< 2 s [88]) in the heated zone (including the reactor zone) followed by rapid quenching of the vapours is crucial to prevent the secondary vapour phase reactions and to obtain higher liquid yields with sufficient bio-oil quality. In CFP of biomass, the secondary vapour phase reactions generally take place after the physical separation of reformed vapours and the catalyst, in the hot zones of the system prior to the condenser. Due to the fact that the catalysed reactions, resulting in a mixture of volatiles (vapours) – these contain gaseous (non-condensable gas compounds such as CO, CO₂, *etc.*) as well as liquid species (*i.e.* aerosols) – do not reach a state of thermodynamic equilibrium, short vapour residence times are necessary to avoid both the overcracking of vapours on the catalyst and the possible secondary reactions (*e.g.* condensation, oligomerization, polymerization) of the desired volatile compounds. Such undesirable vapour phase reactions could be catalysed by the presence of the minerals in the system as well [81]. Hence, to achieve the balance between the time necessary for the completion of catalytic reactions (sufficient contact time for vapour-catalyst surface interactions) and the suppression of unwanted secondary vapour phase reactions, a careful optimization of the carrier gas flow rate is necessary. Carrier gas refers to *e.g.* pure inert gas, recycled oxygen-free flue gas and/or non-condensable gases, or the mixture of these in any combination.

7.3.1.4 Process limitations

7.3.1.4.1 Catalyst circulation

In CFP of biomass, the regeneration (*i.e.* re-activation, oxidative treatment to burn the coke and remove the carbon as CO₂) of the spent catalyst is achieved by recirculating it continuously over a secondary reactor, the ‘regenerator’. By the frequent regeneration, the catalyst should in theory retain most of its original activity and contact the freshly-fed biomass always in an active state [72,86]. The amount of the catalyst continuously circulating within the system must be determined based on the time necessary for a complete regeneration of the spent catalyst in the regenerator. A certain amount of catalyst make-up is indeed necessary due to the possible catalyst losses; these could be due to the irreversible deactivation and/or the attrition of the catalyst. Requirement here is that the catalyst particles should be strong enough to withstand attrition during the several number of successive reaction/regeneration cycles; this should be one of the main focuses in CFP research.

7.3.1.4.2 Catalyst deactivation

Catalyst deactivation is a serious technical and economic problem in CFP of biomass. It is caused by the deposition of coke on the active surface of the catalyst (leading to pore blockage) [234] and further enhanced by the deactivation of the acid sites by the presence of biomass minerals (alkali and alkaline earth metals, AAEMs) [219].

The issue of coke deposition on the catalyst may be eliminated up to a certain level by an effective catalyst design (*i.e.* tuning the physical properties of the catalyst such as the pore size [45]), but also by using an effective and well-optimised reactor design. Such a design should offer high heating rates of biomass, short vapour residence times to prevent re-polymerization reactions, and correct catalyst regeneration techniques. The latter requires optimised procedures involving the temperature level and the duration of the catalyst regeneration (see Chapter 5 in this thesis) [50]. High heating rates of the biomass particles were found to suppress coke formation by homogeneous gas phase thermal decomposition reactions [85] and by heterogeneous reactions on the catalyst particles.

Catalyst poisoning caused by the mineral deposition is irreversible and once totally deactivated, there is no way to benefit from the same catalyst in the process again. Vapour phase reactions are affected by catalyst poisoning and might result in the increased formation of water and gases at the expense of bio-oil yield [29,81] (see Chapter 6 in this thesis). Hence, in a cost-effective CFP process, the direct physical contact between the biomass and the catalyst should be prevented to eliminate the permanent catalyst deactivation due to the mineral accumulation inside the catalyst. This may be possible by the selection of a suitable reactor technology and operation mode (see sections 7.3.1.5 and 7.3.1.6).

7.3.1.4.3 Mixing the catalyst with an inert solid material

In most pyrolysis systems an inert solid material (usually inert sand), of a particle diameter in the range of 200 to 600 μm , is used to enable proper fluidization and recirculation. In continuously operating CFP processes, mixing the catalyst particles with sand, both being circulated continuously over the pyrolysis reactor and the regenerator, seems an attractive option. In a sand-catalyst mixture, sand could act as a binder and improve:

- the external medium-to-biomass heat transfer rates,
- allow varying the ratio of catalyst over sand to adjust the degree of catalysis in relation to the final composition of the CFP-oil,
- could prevent some operational limitations, such as the difficulties in feeding fine catalyst particles through feeding screws (or even through the reactors, *e.g.* auger type).

However, large differences in particle size and/or the density between the catalyst and the inert solid material will lead to segregation [235]. To prevent this, the particle properties of all solid materials inside the system should be kept as close as possible and the catalyst-to-sand mass ratio should be optimised.

7.3.1.5 Operation mode

Based on the location of the catalyst in the process, CFP of biomass can be performed in two different operation modes: *in situ* and *ex situ* [75] (see Fig. 7.1 in this chapter and Fig. 2.1 in Chapter 2).

In the *in situ* mode, the CFP occurs in a single reactor where the biomass feedstock and the catalyst are physically mixed to enable a good contact between the two. The catalyst can be either:

- added directly to the biomass prior to the feeding by *e.g.* wet impregnation. Since it would be impossible for a heterogeneous catalyst to catalyse the thermal decomposition of lignocellulosic biomass itself, this could be beneficial to control the initial biomass decomposition catalytically and to decompose the biomass in a selective way [231].
- or just mixed with the biomass in pure form or in the form of a mixture with an inert solid material (usually inert sand). However, the heat transfer to the biomass particles may differ when the heat capacities of the catalyst and the inert solid material are different.

In both options, catalysts will be active at the operating temperature of the pyrolysis reactor and immediately attack the volatiles released from the biomass particles.

When the in situ processing mode is applied in systems involving a continuous circulation of the catalyst, the accumulation of biomass originated ash (minerals, *i.e.* alkali and alkaline earth metals) in the catalyst material during the successive use of the same catalyst sample [218,219] should be prevented. The ash could be removed from the catalyst either:

- by the removal of char (containing the vast majority of ash) prior to the regeneration step. This allows the char-free but coke-rich catalyst particles to be regenerated in the absence of ash.
- or by the removal of ash after the regeneration step. This involves the burning of char and the coke-on-catalyst together and thus results in a homogeneous solid mixture of ash+catalyst. Cyclone(s) can be installed at the outlet of the regenerator to separate the ash and the regenerated catalyst. However, similar particle properties (*e.g.* size, density) of the two may limit the efficient separation of the ash.

Both options are practically hard to implement. Separation of char before the catalyst regeneration step seems as the most feasible one. Char separation has been applied in bubbling fluid bed pyrolysis [236] but is technically more difficult to achieve in a transported bed technology. However, it deserves to be considered for the future CFP installations. To this end, char separation through sieves, high temperature resistant electrostatic precipitators, and/or ceramic filters could be explored.

In the ex situ mode, the primary pyrolysis vapours produced inside the first reactor (*i.e.* non-catalytic pyrolysis reactor) are carried through a secondary reactor (*i.e.* ex situ reactor) where they are contacted with the catalyst. The possibility of independent adjustment of reactor temperatures and secondary input of gas (*e.g.* hydrogen) to the ex situ reactor may assist controlling the product distribution and selectivity. The most important advantage of the ex situ CFP is the periodic regeneration of the spent catalysts (refers to the removal of the coke on catalyst by oxidative treatment) that can be conducted in absence of the ash containing char, and thus prevent the accumulation of biomass ash [81,218] in the catalytic reactor. A disadvantage of the presence of a catalytic reactor in the vapour stream to the condenser could be the corresponding increase in the vapour residence time which is known to promote thermal cracking and a loss in condensable compounds. To prevent these

secondary reactions in the vapour phase, the vapour residence time in between the two reactors should be kept short. For that reason, the length of the connecting pipelines in between these two reactors should be as short as possible and thermally insulated.

Ex situ configurations seem technically the most challenging, and probably have the highest capital cost due to the presence of an additional regenerator and an ex situ reactor (and its auxiliary components such as cyclone(s), *etc.*). From a long-term operational cost point of view however, this processing mode is more appropriate for CFP of biomass. The activity of the catalyst is eventually conserved over a much longer period because it is not in contact anymore with the biomass minerals (no risk of catalyst poisoning by minerals). This allows the catalyst to be re-used larger number of reaction/regeneration cycles than that of in an in situ operation. However, the quantity and the quality of the CFP-products obtained in the ex situ processing might differ (in terms of the yields of CFP-oil and the coke-on-catalyst) from that of in situ processing [100] (see Chapter 3 in this thesis); this should be kept in mind and researched thoroughly.

7.3.1.6 Reactor technology

7.3.1.6.1 Reactor technology suitable for in situ operation

A transported bed system with a riser reactor and a regenerator for the continuous catalyst regeneration can be considered (Fig. 7.2). This approach has been applied for in situ CFP of biomass both for research and commercial purposes [32,150]. The operation is similar to that of fluid bed catalytic cracking of crude petroleum oil (FCC), where commercially available small ($d_p \leq 80 \mu\text{m}$) and light ($\rho_p \sim 1500 \text{ kg/m}^3$) catalyst particles are recirculated through a riser reactor (cracking) and a turbulent fluid bed regenerator (coke burn-off). In FCC units, the cracking takes place in a riser reactor that is typically operated at linear gas velocities of 15 m/s. The catalyst is transported at a slightly lower velocity (slip velocities ranging between 1 and 10 m/s, depending on the density of the catalyst) and its minimal residence time in the riser is typically 2 to 3 seconds ($L_{\text{riser}} = 20\text{--}30 \text{ m}$) [237]. Here, the question to be discussed is whether or not a riser would be a suitable reactor for CFP of biomass. Although strictly depending on the length of the riser reactor and the velocity of the transported particles, such a configuration would offer relatively short residence times to the catalyst and the biomass particles. That may be suitable for very fine biomass particles ($<0.5 \text{ mm}$ particle diameter) which can be devolatilized completely within a few seconds. However, for the biomass particle size range typically used in fast pyrolysis ($1 < d_p < 5 \text{ mm}$) the required pyrolysis times are much longer (10–30 s). They cannot be converted completely in a FCC riser reactor. To improve the external medium-to-solid heat transfer rates, the catalyst could be mixed with an inert solid material (*e.g.* fine sand) having a higher heat capacity than that of the catalyst. To achieve similar circulation rates of the catalyst and the inert particles, the particle properties of these should be similar. A uniform circulation is possible by applying turbulent or fast fluidisation regimes that prevents the extensive segregation of the recirculated solids. However, if the particle properties (*e.g.* densities, sizes) of the inert solid material and the available catalyst are too far apart one could rely on using a pure catalyst. One could consider applying a turbulent fluid bed as the CFP reactor, instead of a riser. This may offer sufficient time for biomass particles of a more realistic size to devolatilize.

However, due to the rapid deactivation, most of the catalyst inventory would then be ‘dead’ and inactive. An additional problem of using an FCC-like system for CFP by introducing biomass (dust) is the direct contact of the catalyst with the ash containing biomass. The separation of char particles prior to their entrance to the regeneration chamber is a must. Otherwise, the accumulation of char within the system, and thus the irreversible deactivation of the catalyst by the accumulated ash, is inevitable. However, the separation of very small char particles from the catalyst particles having similar sizes is not possible. A solution would be to leach the biomass feedstock before being fed to the system; however, technical and economic benefits of this operation with respect to potential catalyst losses should be well considered.

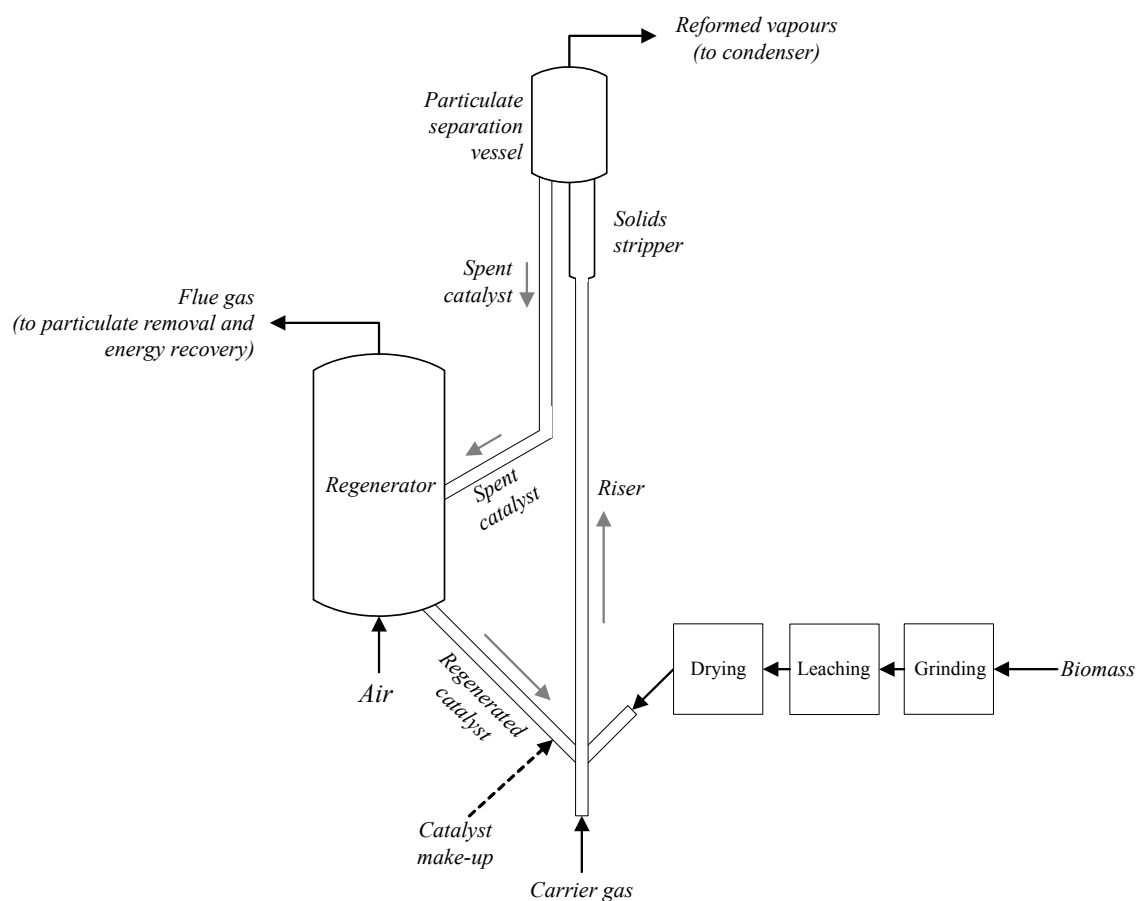


Fig. 7.2. Scheme of the FCC-like circulating system applied for in situ catalytic fast pyrolysis of biomass.

Besides the FCC-like systems, auger (screw) reactors can also be considered for in situ CFP of biomass (Fig. 7.3) due to the high heating rates they offer when the biomass particles are heated by an externally supplied solid material (*e.g.* sand, catalyst, or a sand-catalyst blend). They are compact and robust, require little (or no) carrier gas, offer good flexibility in feedstock size and properties, and may have biomass processing capacities from 50 to 100 tons/day [95–97]. In auger reactors, the biomass residence time is a function of the length and the turning frequency of the auger screw. Hence, unlike CFB systems, bigger biomass particles (~5 mm) can be used and longer biomass residence times can be achieved for a complete devolatilization. This would help to achieve a better efficiency in char separation as well. The most important advantage of auger reactors is that they may offer a better control of the catalyst-to-biomass ratio. However, the transportation of very fine catalyst particles through the feeding and the auger screws might be a technical barrier. As mentioned in section 7.3.1.4.3, feeding a pre-mixed catalyst-inert solid material blend to this reactor is beneficial, not only for a better performance in feeding and solids transportation, but also to prevent the particle segregation. Besides, the active catalyst could become deactivated before reaching to the end of the auger screw; this could be prevented by feeding the active catalyst through multiple insertion points (see Fig. 7.3). The number of these insertion points could depend on the length of the auger screw and/or the deactivation rate of the catalyst. The latter is a function of catalyst-to-biomass ratio. The list of the main characteristics of the proposed reactor designs is shown in Table 7.1.

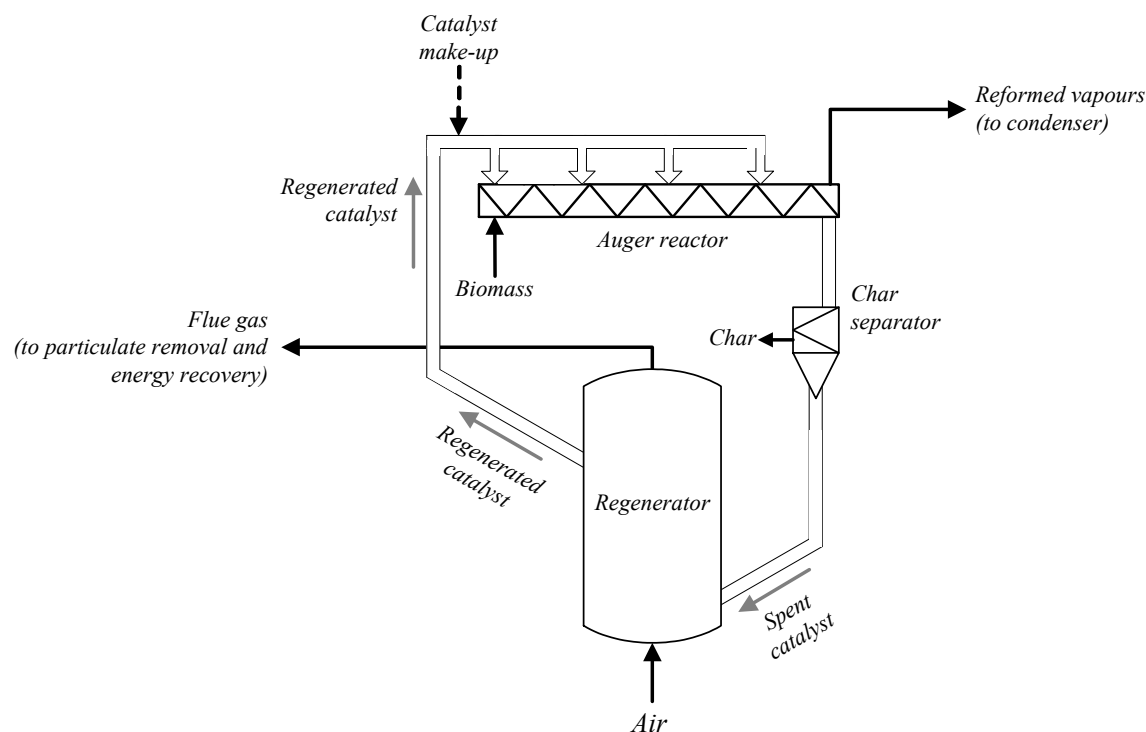


Fig. 7.3. Scheme of the auger reactor technology for in situ catalytic fast pyrolysis of biomass.

Table 7.1. The list the main characteristics of the proposed reactor designs.

<i>Reactor type</i>	FCC-like with a riser	Auger
<i>Operation mode</i>	in situ / ex situ	non-catalytic / in situ
<i>Biomass residence time</i>	min. 2–3 s ^a	N/A ^c
<i>Vapour residence time</i>	min. 2–3 s ^a	N/A ^d
<i>Contacting pattern</i> ^b	co-current	cross- / co-current
<i>Bed material</i>	pure catalyst	catalyst/sand mixture
<i>Regeneration method</i>	turbulent fluid bed regenerator	turbulent fluid bed regenerator
<i>Solids transport mechanism</i>	carrier gas + gravity	mechanical + gravity + solid pumping

^a Depending on the length of the riser and the velocity of the carrier gas.

^b Contacting pattern of primary pyrolysis vapours and the catalyst.

^c Is a function of the length and the turning frequency of the auger screw.

^d Is a function of the velocity of the vapours/carrier gas.

7.3.1.6.2 Reactor technology suitable for ex situ operation

In ex situ CFP of biomass, any type of proven fast pyrolysis reactor, capable of being run continuously, can be used as the non-catalytically operating fast pyrolysis reactor (*e.g.* fluid bed, auger, rotating cone). The main purpose of this primary fast pyrolysis reactor is to allow a maximum degree of biomass devolatilization, possibly with longer biomass residence times (*e.g.* auger reactor). It should have a design that allows shorter vapour residence times to prevent secondary vapour reactions. Generated primary pyrolysis vapours are then transferred immediately to the ex situ reactor; that could be the riser of a circulating catalyst system (Fig. 7.4). Similar in FCC units in petroleum refineries where the hot petroleum vapours are fed to the riser section of the system, hot primary pyrolysis vapours could benefit from the same idea. This option would prevent the physical contact of biomass ash and the catalyst with each other, and thus the catalyst deactivation due to the ash accumulation on the catalyst could be completely prevented. Moreover, the mismatch in time-scale of biomass devolatilization and vapour reforming/catalyst deactivation is avoided.

Alternatively, instead of relying on commercially available catalysts, one could consider to design a dedicated catalyst for hot vapour treatment, based for instance on monoliths or packed reactor columns. While the risk of plugging may be limited, the operation of a monolithic reactor may have many other serious problems to overcome, related for instance to the requirement of frequent regeneration.

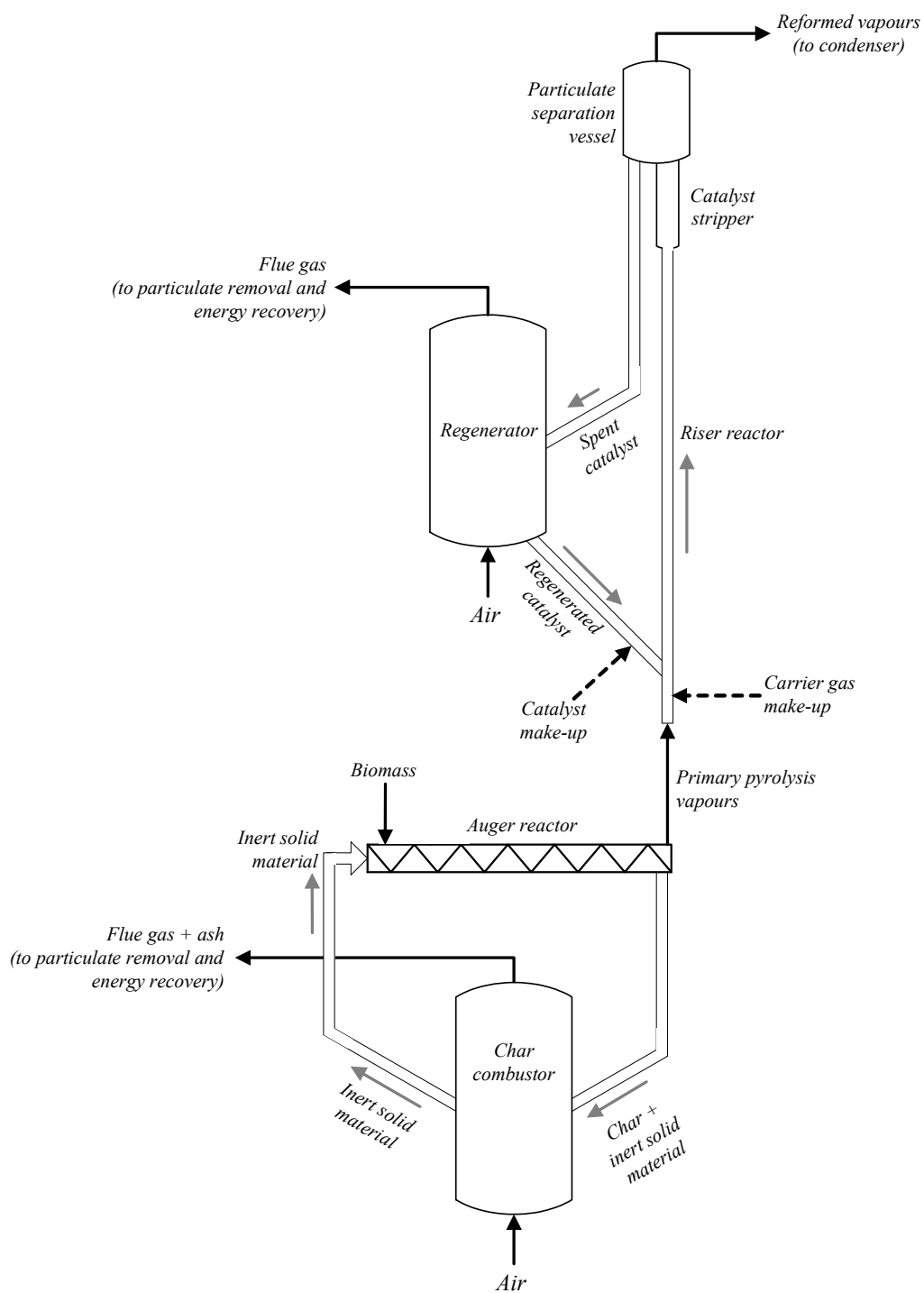


Fig. 7.4. Scheme of a proposed continuously operating ex situ process configuration for catalytic fast pyrolysis of biomass. The fast pyrolysis reactor is an auger type while the ex situ reactor is a FCC-like circulating system.

7.3.2 Heat integration

The primary decomposition reactions in biomass pyrolysis (*i.e.* the breakdown of cellulose, hemicellulose and lignin into vapours) are endothermic – and these reactions are not affected by the presence of a heterogeneous catalyst. Further reactions in the vapour phase, both those in the presence of a heterogeneous catalyst (catalytic pyrolysis) as well as those without (non-catalytic pyrolysis), could be endothermic or exothermic. A certain degree of energy input is required to heat the cold biomass feedstock up to the reaction temperature (including moisture evaporation and biomass devolatilization) and for the multitude of individual endothermic chemical reactions that occur during pyrolysis (*e.g.* dissociation reactions of biomass bio-polymers; cellulose, hemicellulose and lignin). The challenge for engineers is to configure pyrolysis technologies allowing for an efficient heating of the feedstock while minimising energy losses through a proper heat recovery.

The degree of heat integration highly affects the continuity, economy and efficiency of the process. In a pyrolysis process, the combined effect of heating the feedstock and supplying the reaction heat is defined as the heat for pyrolysis [238]. Being an essential design parameter for a pyrolysis process, it was estimated to be 1.5 MJ/kg for dry (~10 wt.% moisture) pine or beech wood [21]. This energy can be generated in a combustor (regenerator) from the pyrolysis by-products (char, coke on spent catalyst and/or non-condensable gases) and/or a waste heat boiler in which the non-condensable gases are burned with air at a constant temperature. The type and the amount of by-products to be utilized for the energy generation should be well-defined for an energy efficient process. Any surplus heat can be used to produce steam and/or electricity for internal use in the first place, or for sale if necessary. Low temperature waste heat is still useful for drying of the biomass feedstock to the required moisture level of *ca.* 10 wt.%.

To provide the process heat necessary for CFP, burning an amount equal to the 12 % of the carbon of the biomass feedstock was calculated to be sufficient [85]. In conventional fast pyrolysis, char is typically about 15 wt.% of the products but contains *ca.* 25 % of the energy of the biomass feed [29] and is more than enough to run the pyrolysis process [21]. On the other hand, non-condensable gases contain *ca.* 5 % of the energy in the biomass feed [28], which alone is not sufficient to provide the heat for pyrolysis. When the char is used to drive the process energetically, a part of these gases could be recycled to the reactor. Non-condensable gases (contains a certain amount of H₂) have the potential to be consumed by the catalyst for hydrocarbon production, and could thereby suppress the coke formation and increase the retention of hydrogen in the liquid product. Alternatively, they can be burned in a waste heat boiler to contribute to the energy surplus or can be fed to a hydrogen plant as a feedstock as well [71]. In order to keep the CFP process as economical as possible, it is preferred to recycle all the catalyst back into the reactor after a regeneration step. As mentioned earlier, the catalyst can be in its pure form or mixed with an inert solid material (*e.g.* sand) with similar particle properties to that of the catalyst. One benefit of the recirculation is that the catalyst (or the catalyst-inert solid material mixture) remains hot and thus transfers the heat to the freshly introduced biomass. Another benefit is that, the expensive heterogeneous catalyst can be used multiple times after being regenerated (successive reaction/regeneration steps).

Table 7.2 shows the energy yields in the CFP product fractions obtained from three different setups with respect to different process modes. The energy yields were calculated based on the heating values and the yields of catalytic fast pyrolysis products and the heating value of the biomass feedstock. Only the results obtained in continuously operated setups, wherein (H-)ZSM-5 catalysts were used, were included. Paasikallio *et al.* [219] performed the CFP of pine sawdust in VTT's 20 kg·h⁻¹ Process Development Unit using spray dried HZSM-5 catalyst. Based on the provided data included in their article, the overall energy yield of the process was calculated to be more than 92 %. This value excludes the non-available data for non-condensable gases. In their work, *ca.* 47 % and 45 % of the energy in the feedstock was recovered in the CFP-oil and in the char/coke, respectively. Iliopoulou *et al.* [239] performed in situ CFP of a commercial lignocellulosic biomass (Lignocel HBS 150-500) originating from beech wood with ZSM-5 catalysts (diluted with a silica-alumina matrix). This continuously operated setup included a circulating fluidized bed reactor. Based on the given data, the overall energy yield was calculated to be 93 %, of which 53 %, 3 %, and 37 % of the energy is distributed to the CFP-oil, non-condensable gases, and char/coke, respectively. It is important to notice that, the yields of char and coke were reported as combined in these studies. Therefore, it is not possible to comment on the individual energy contents of char and coke. Moreover, this char/coke combination was assumed to be 100 % carbon; but in fact both char and coke contain significant amounts of hydrogen and oxygen in their structure and the resulting HHV (higher heating value) is lower than when assumed a pure C-based solid product. This could cause some errors in the calculation of the energy balances. Yildiz *et al.* [100] performed in- and ex-situ CFP of pine wood with ZSM-5 based acidic zeolite in a continuously operated lab-scale setup. The setup consists of an auger reactor as the in situ reactor and a moving bed (co-current) reactor as the ex situ reactor. The calculated overall energy yields are 72 % and 80 % for in situ and ex situ operations, respectively. The non-closure in the energy balance is presumably caused by the analytical errors in the sampling for elemental analyses of the collected liquids. However, the energy yields of non-condensable gases, char, and coke provide clear indications regarding the heat integration of the system. In both operation modes, non-condensable gases contain 4-5 % of the energy. On the other hand, char contains 27 % and 33 % of the energy for in situ and ex situ modes, respectively. In both operational modes, coke contains 8 % of the energy in the biomass. These results show that, the combustion of by-products of the CFP process is more than sufficient to run the process autothermally.

Table 7.2. Heating values and the yields of catalytic fast pyrolysis products obtained from previously published experimental data and calculated energy balances with respect to different process modes (*a.* in situ, and *b.* ex situ).

a. Results of *in situ* experiments performed in continuously operated setups using (H)-ZSM-5 catalysts:

- Paasikallio et al [219], circulating fluidized bed reactor with 20 kg/h biomass intake:

	Heating values [MJ/kg]	Yields [wt.% on feed]	Energy balance			
			MJ/kg		Energy yield, %	
			In	Out	In	Out
Pine wood	20.4	-	20.4		100	
CFP-oil	29.7 ^a	32		9.5		46.6
Water	-	19 ^b		-		-
NCG's	N/A	21		N/A		N/A
Char/Coke	34 ^{d,f}	27		9.2		45.0
Total		99	20.4	18.7	100	91.6

- Iliopoulou et al. [239], circulating fluidized bed reactor with 0.33 kg/h biomass intake:

	Heating values [MJ/kg]	Yields [wt.% on feed]	Energy balance			
			MJ/kg		Energy yield, %	
			In	Out	In	Out
Beech wood	16.4 ^a		16.4		100	
CFP-oil	34.1 ^a	25.4		8.7		52.8
Water	-	23.4 ^b		-		-
NCG's	~1.5 ^c	33.3		0.5		3.1
Char/Coke	34 ^{d,f}	17.9		6.1		37.1
Total		100	16.4	15.3	100	93.0

- Yildiz *et al.* [100] (see Chapters 3 and 4 in this thesis), auger reactor with 0.2 kg/h biomass intake:

	Heating values [MJ/kg]	Yields [wt.% on feed]	Energy balance			
			MJ/kg		Energy yield, %	
			In	Out	In	Out
Pine wood (a.r.)	16.8 ^a		16.8		100	
CFP-oil	33.6 ^a	16.3		5.5		32.6
Water	-	34 ^b		-		-
NCG's	3.1 ^c	24.7		0.77		4.6
Char	28.2 ^d	16.2		4.6		27.2
Coke	18.5 ^{d,e}	7.1		1.31		7.8
Total		98.3	16.8	12.1	100	72.2

Table 7.2. continued.

b. Results of an *ex situ* experiment performed in a continuously operated auger reactor using a ZSM-5 catalyst:

- Yildiz *et al.* [100] (see Chapters 3 and 4 in this thesis), auger reactor with 0.2 kg/h biomass intake as the fast pyrolysis reactor and moving bed reactor (co-current flow) as the *ex situ* catalytic reactor:

	Heating values [MJ/kg]	Yields [wt.% on feed]	Energy balance			
			MJ/kg		Energy yield, %	
			In	Out	In	Out
Pine wood (a.r.)	16.8 ^a	-	16.8		100	
CFP-oil	34.1 ^a	16.7		5.7		33.9
Water	-	34.2 ^b		-		-
NCG's	3.0 ^c	23.9		0.72		4.3
Char	30 ^d	18.7		5.6		33.4
Coke	18.5 ^{d,e}	7.1		1.3		7.8
Total		100.6	16.8	13.3	100	79.4

^a Calculated based on Milne formula: $\text{HHV} = 338.2 \times \text{C} + 1442.8 \times (\text{H} - (\text{O}/8))$ [MJ/kg]. In Milne *et al.* [196]

^b Based on the results of Karl-Fischer analyses.

^c The composition of NCG's are derived from micro-GC analyses. The heating value of NCG's was calculated by: $\text{LHV}_{\text{NCG}} = (30.0 \times \text{CO} + 25.7 \times \text{H}_2 + 85.4 \times \text{CH}_4 + 151.3 \times \text{C}_n\text{H}_m) \times 4.2$ and converted into MJ/kg. In Ioannidou *et al.* [190]

^d $\text{HHV}_{\text{char}} = 0.34 \times \% \text{C} + 1.4 \times \% \text{H} - 0.16 \times \% \text{O}$, [MJ/kg]. In Ioannidou *et al.* [190]

^e Coke refers to coke on catalyst. The elemental composition of coke was obtained (the given values were averaged) from Williams and Horne [195].

^f Char/coke is assumed to be 100 % carbon.

N/A: Not available

7.3.3 Process alternatives

The distributed thermochemical processing model based on fast pyrolysis of the feedstock at its source, and subsequent centralized product collection/utilization elsewhere, requires easily operable, small to medium scale, on-site process equipment [57]. The core elements in a continuously operating CFP factory are: pre-treatment unit (feedstock grinding, leaching, and drying), feedstock and catalyst conveying systems (including recycling systems), the reactor, heat production systems (combustors, boilers), vapour condensation system (condenser), and char/ash removal/separation systems (*e.g.* cyclones, filters) [26]. Catalytic fast pyrolysis essentially involves a reactor technology (see section 7.3.1.6) which allows the catalyst to be regenerated and recirculated. Heat generation within the CFP process can be attained by various process alternatives as shown in Fig. 7.5. This figure contains schematic drawings of some possible process alternatives for CFP of biomass (a, b, c and d) based on the considerations above:

- a. The process operates in in situ mode. The solid stream exiting from the CFP reactor is burned with air in a regenerator to revive the catalyst and deliver the heat for pyrolysis. Depending on the used reactor technology, this solid stream is composed of spent catalyst or a spent catalyst-sand mixture (both contain a considerable amount of heterogeneous coke), and char. The regenerated catalyst (or the catalyst-sand mixture) is recycled back to the CFP reactor. Steam pipes are installed in the regenerator in order to control the regeneration temperature and produce steam from the energy surplus (Q_{steam}). Special attention should be given to the accumulation of biomass derived minerals (AAEMs) within the system. A solution for this may be to wash the biomass feedstock with water and/or an acidic solution (*i.e.* leaching) and remove the minerals in this way before the biomass is fed to the reactor. The pyrolysis vapours leaving the reactor through the cyclone(s) are quenched in the condenser to form the liquid product. If necessary, the liquid product can be filtered in order to remove the fine particulates. This liquid is fed through a liquid phase separator (*e.g.* centrifuge) wherein the aqueous and the organic liquid phases (CFP-oil) are separated. Aqueous phase can be used for biomass leaching or can be used for instance as a feed for (supercritical water) gasification or reforming units. The non-condensable gases (NCG) are fed to a waste heat boiler wherein they are burned together with the regenerator off-gases and excess air to produce energy ($Q_{\text{waste heat boiler}}$). Alternatively, a part of these gases can be recycled to the reactor – but the pressure increase in the system should be well-controlled. The energy produced in this configuration may exceed the amount of energy necessary for the process. In that case, the surplus amount of the energy (in the form of steam or electricity) can be sold to the market.
- b. The process operates in in situ mode. Char is collected via a char separator rather than being burned in the regenerator and considered as a secondary product of the process that is sold on the market as a solid fuel or as a biochar for soil improvement. This separation prevents the accumulation of the biomass ash within the system. In the regenerator, the char-free spent catalyst, which contains a considerable amount of heterogeneous coke, is burned with air. The regenerated catalyst is then recycled to the CFP reactor. The non-condensable gases leaving the condenser and regenerator off-gases leaving the regenerator are fed to a waste heat boiler to deliver the heat for pyrolysis. In case of an energy deficit, some of the char and/or biomass feedstock can be burned. However, this would require a separate combustor, because ash containing char and biomass cannot be burned together with the catalyst. It would make the system more expensive. Alternatively, burning some excess natural gas in the waste heat boiler could be considered.
- c. The process operates in in situ mode. All produced non-condensable gases are fed to the regenerator where they are combusted. This option eliminates the costs for the installation of a waste heat boiler. Char is collected and considered as a product of the process. The spent catalyst carrying the heterogeneous coke is transferred to the regenerator where the coke combustion contributes (together with the non-condensable gas combustion) to the production of process heat. The energy that is

acquired from the hot exhaust gases ($Q_{\text{exhaust gases}}$) can be added to energy surplus or used for the drying of the feedstock materials (particularly in case the biomass feedstock that is very wet).

- d. The process operates in ex situ mode. The stream of solids (sand and char) exiting from the primary fast pyrolysis reactor (non-catalytic) is burned with air in the combustor to deliver the heat for pyrolysis. Ash is removed by the flue gas from the combustor passing through a cyclone and the ash-free sand is recycled back to the pyrolysis reactor. The primary pyrolysis vapours leaving the reactor are fed to the catalytic reactor (ex situ reactor). The solid stream exiting from the catalytic reactor which is composed of spent catalyst (including the heterogeneous coke) is burned with air in the regenerator to deliver the heat for pyrolysis. Regenerated catalyst (ash-free) is recycled back to the catalytic reactor. The non-condensable gases leaving the condenser, as well as the combustor and regenerator off-gases are fed to a waste heat boiler to deliver the heat for pyrolysis. Optionally, a part of the non-condensable gases can be recycled to the reactor(s). If the produced amount of energy exceeds the required heat for pyrolysis, the surplus amount of the energy (in the form of steam or electricity) can be sold to the market.

Based on the process alternatives discussed above, a process scheme for the CFP of woody biomass is proposed in Fig. 7.6. In this scheme, ex situ processing mode is selected in a way that the catalyst and the vapours are practically not affected from the biomass originated minerals.

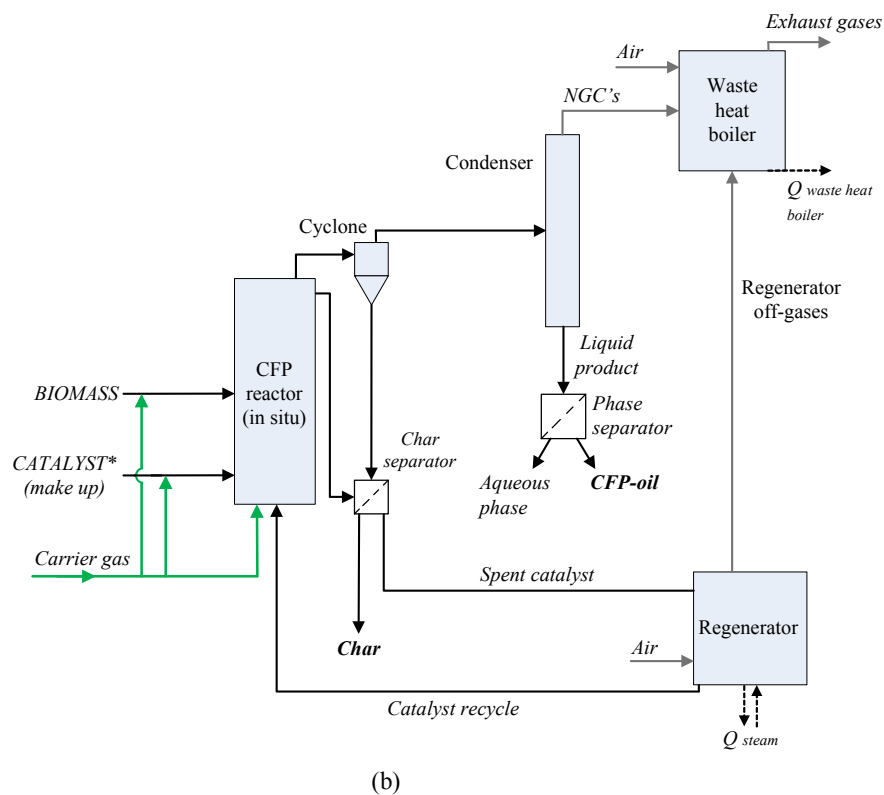
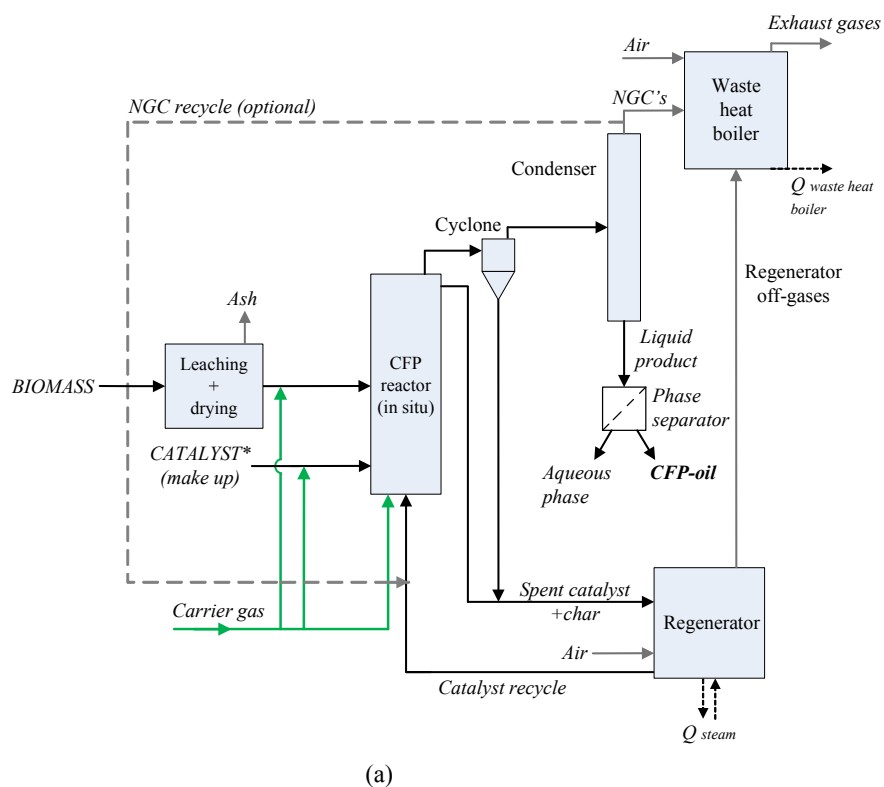
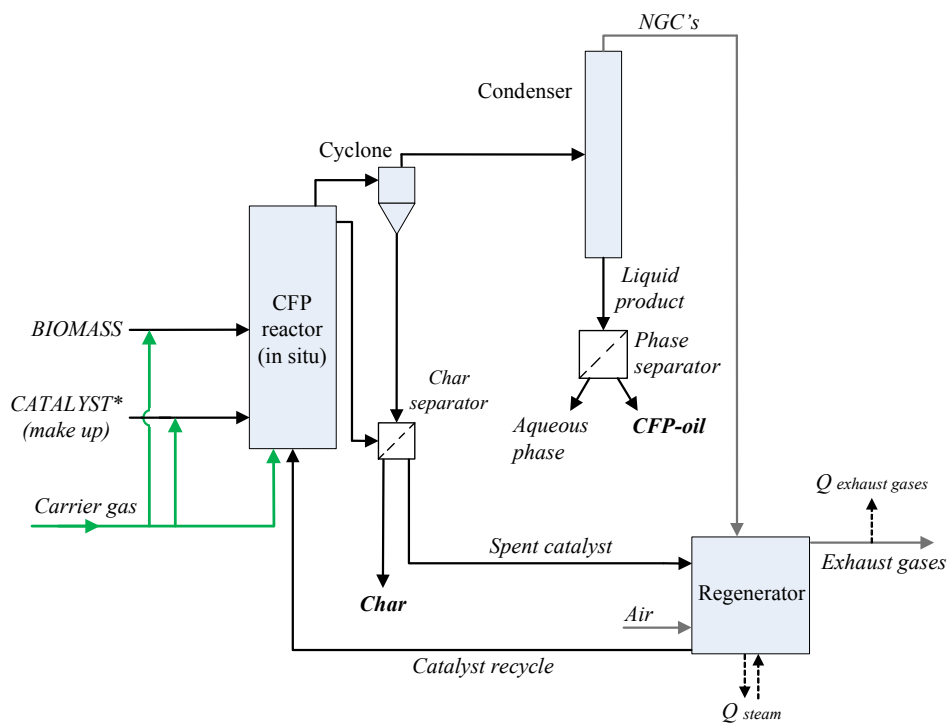
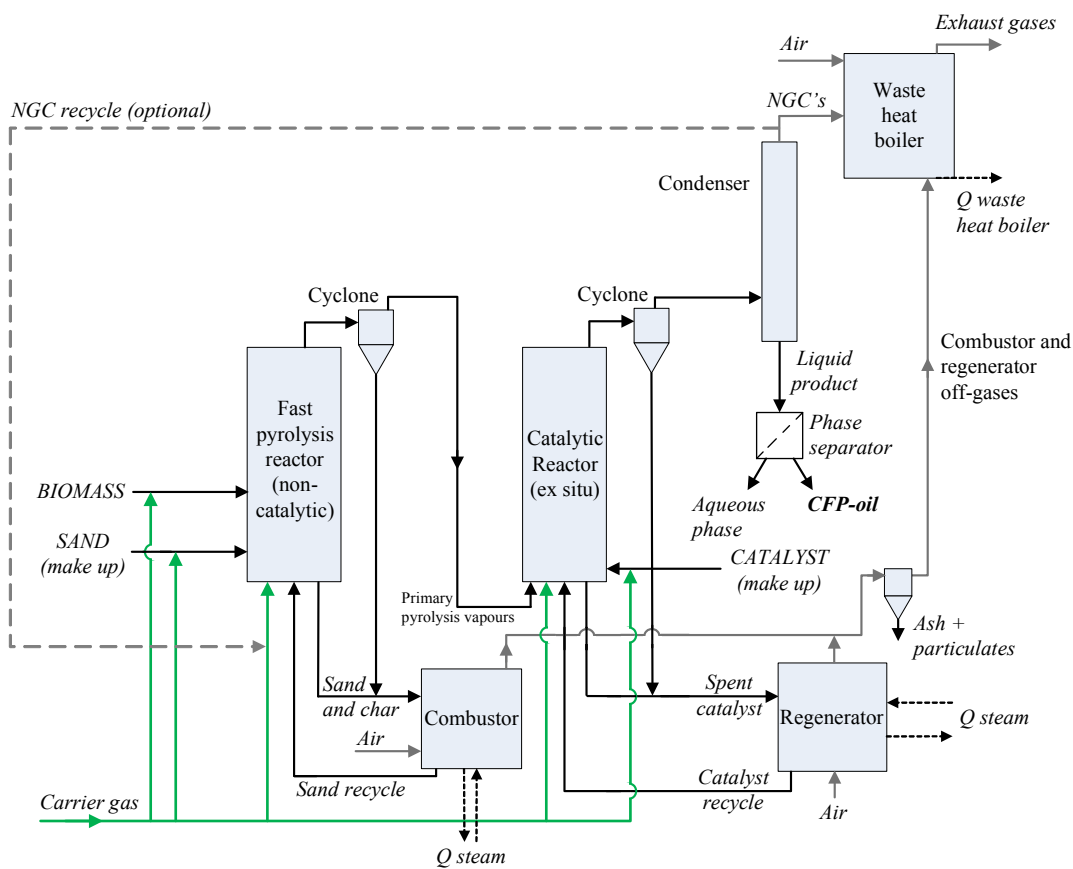


Fig. 7.5. Considered continuously operated process options for CFP. (a), (b), (c): in situ process alternatives, (d): ex situ process alternative.

* Depending on the selected reactor technology, the catalyst can be mixed with inert solid material.



(c)



(d)

Fig. 7.5. continued.

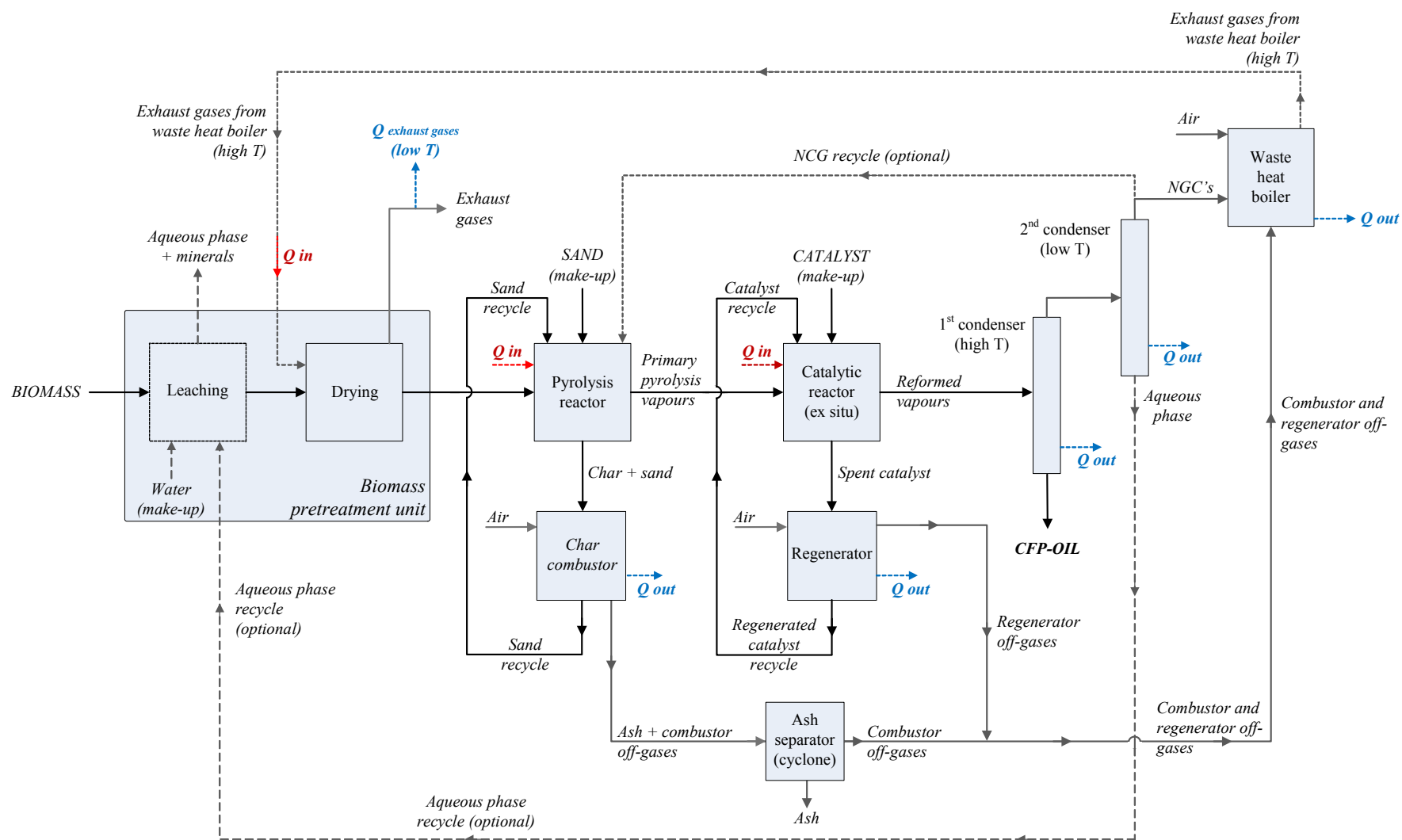


Fig. 7.6. Proposed scheme of a CFP process for low-ash (<1 wt.%) containing woody biomass.

7.4 Conclusions

While the bulk of the past research concerning the catalytic fast pyrolysis (CFP) of biomass has been focussed on catalyst screening, there is an urgent need for process design related research addressing key issues like the catalyst type suited to the requirements of the continuous processes, the most suitable reactor technology, and the way of heat integration of the process. In order to obtain the target products in CFP of biomass with desired yields and compositions, the process conditions such as the processing mode (*e.g.* in situ, ex situ), the reaction temperature, heating rate and the residence time of the biomass feedstock, catalyst-to-biomass ratio, and the vapour residence time need to be optimized precisely. Moreover, a careful selection of the biomass feedstock (including its particle size, moisture and ash contents), and the type of the catalyst (*e.g.* resistance to deactivation) is essential.

In CFP of biomass, the main problem to be dealt with is the presence of the biomass originated alkaline ash which destroys and physically swamps any catalyst utilized in the process. Practically, the direct physical contact between the catalyst and the biomass must be prevented in order to achieve a successful operation. Hence, prior to scaling up this technology to a commercial level, this particular problem should be clearly identified and solved. One suggestion might be the utilization of the ex situ processing mode wherein a separate catalytic reactor is used for reforming the primary pyrolysis vapours. In this way, the periodic regeneration of the spent catalysts (refers to the removal of the coke on catalyst by oxidative treatment) can be conducted in the absence of char (contains the vast majority of the biomass ash), and thus prevent the accumulation of biomass originated ash in the catalytic (ex situ) reactor.

From an economic point of view, CFP installations should be self-sustaining while any surplus energy should be used as efficiently as possible. This requires proper heat integration. To this end, the utilization of any by-products (*i.e.* char, coke on catalyst, non-condensable gases) for the heat generation is necessary. More research is needed in order to understand the effects of different process parameters and to optimize heat balance of the CFP system. Careful design of the product recovery is needed to ensure product stability and mitigate fouling. Moreover, effective removal of solids from the product liquid is crucial to overcome the negative effects on downstream integration.

Summary, main conclusions, and remarks

Crude pyrolysis oil (bio-oil), the liquid product obtained from non-catalytic fast pyrolysis of lignocellulosic biomass, is a mixture of hundreds of different, oxygen containing organic compounds. The presence of oxygen in bio-oils (*ca.* 35–40 wt.%) is commonly believed to be the origin of problems including its high water content (15–30 %), corrosiveness (pH of 2–3), relatively low heating value compared to fossil fuels (*ca.* 17 MJ/kg), poor volatility, and high viscosity (35–1000 cP at 40 °C). However, while realizing that second generation bio-fuels may contain significant amounts of oxygen (like in ethanol or methanol), it is postulated here that not the oxygen itself is a problem, but the way in which the oxygen is present in the bio-oil. If the quality of the bio-oils should be steered, whether or not in combination with a certain degree of oxygen removal, that would include a selective transformation of the oxygen functionalities into ‘desired’ or acceptable ones like alcohols and ethers. Undesired chemical compounds are those with highly reactive functional groups, *e.g.* carboxylic acids, aldehydes, ketones. A key issue to be learnt, by proper bio-oil analysis, is the quantity of these oxygen containing groups present in the bio-oil, and how their presence can be changed selectively. Certain combinations of different oxygen functionalities like acids/alcohols or alcohols/aldehydes are also undesired as they can easily lead to polymerization reactions. All this leads to the conclusion that steering of the oxygen functionalities should be the main concern in upgrading of pyrolysis oils, next to a reduction of the oxygen content.

In any scenario for the production of upgraded bio-oils from biomass materials, the goal is usually to produce either high yields of transportation fuel compounds (*e.g.* aromatics, olefins) and specialty chemicals (*e.g.* phenolics), or just a drop-in refinery feedstock to be blended with the feed streams of existing petroleum refineries. It has already been recognized in the early days of fast pyrolysis R&D that the application of catalysis could be of major importance in controlling the quality and the chemical composition of the bio-oil. For this purpose catalytic fast pyrolysis (CFP) of biomass, which is a single step process based on the use of heterogeneous catalysts in the fast pyrolysis process, can be put in service. In CFP of biomass, the catalysts react with biomass derived primary pyrolysis vapours at atmospheric pressure. The process intends to improve the quality of the liquid product by: *i*) the cracking of high molecular weight compounds to smaller ones; this can reduce the average molecular weight of the liquid product, *ii*) steering the vapour phase reactions with respect to rates and selectivity. Hence, the reactions that cause a change in oxygen functionalities can be induced, while the acidity, density, and the viscosity of the liquid product (predominantly organic phase, *i.e.* CFP-oil) are together modified. This way, the liquid product can be deoxygenated to a great extent while its stability and calorific value is increased. It would thus become more

similar in chemical composition to current gasoline and diesel fuels than the conventional crude bio-oil.

While the literature on the catalytic fast pyrolysis of biomass –mainly focussed on catalyst screening– is rapidly expanding, there is an urgent need for the translation of laboratory results to viable process concepts and pilot plant trials by addressing key issues like the most suitable processing mode, the reactor technology, and the way of heat integration of the process. The present thesis discusses the catalytic fast pyrolysis of lignocellulosic biomass in a process oriented way that may initiate a useful process technology development in the near future. The final goal is to come up with recommendations and suggestions on how to realize this technique at a commercial/industrial scale. That requires a better understanding of the precise effects of the essential process parameters (*e.g.* processing mode; in- or ex situ) and design elements (*e.g.* reactor type, catalyst type) on the one hand, and definitions and outcomes of possible obstacles (*e.g.* successive regeneration of the catalyst, effect of biomass ash) on the other.

The purpose of CFP of biomass

The main target of catalytic fast pyrolysis of lignocellulosic biomass is to selectively transform the liquid product by cracking and deoxygenating it as much as needed while minimizing the coke formation on the catalyst. Depending on the catalysts used and the process conditions applied, varying degrees of deoxygenation can be achieved via simultaneous decarbonylation (CO rejection), decarboxylation (CO₂ rejection) and dehydration (H₂O forming) reactions. Obviously, oxygen removal via dehydration is in turn less desirable than CO₂ or CO formation in order to preserve the highly energetic carbon–hydrogen bonds in the bio-oil constituents and also to preserve hydrogen for the catalyzed hydrocarbon forming reactions. In the case of decarbonylation, a single carbon atom is consumed to remove each oxygen atom, whereas the removal of oxygen in the form of CO₂ would be the most preferable route because in decarboxylation two oxygen atoms are removed while only a single carbon atom is consumed. Complete deoxygenation however, would result in producing only hydrocarbons (or just carbon in the worst case) at a very low yield. Hence, catalysis should be applied rather for the stabilization of the liquid product by controlling the molecular size distribution (cracking) and steering the oxygen functionalities, resulting in the production of certain fuel compounds or chemicals (aromatics, alkanes, phenols, alcohols, *etc.*) in the produced liquid.

The process yields a liquid product composed of two phases, *viz.* an aqueous phase (rich in water and acids) and a heavy phase rich in (partially) deoxygenated organic compounds (*i.e.* CFP-oil). In principal, the latter can be used to co-feed a fluid catalytic cracking unit (FCC) in existing petroleum oil refineries; further (co-)processing in such a unit would at least require a significant degree of deoxygenation and a good miscibility with the regular refinery feedstock. That would enable the production of drop-in hydrocarbon fuels without building a separate bio-oil refinery. Hence, in a CFP process, consideration should be given to the production of liquid intermediates with improved physical and chemical properties instead of finished fuels.

It should be noticed that the development of CFP is in its infancy in comparison with other thermo-chemical technologies (*e.g.* gasification), and the required product specifications are still fairly undefined. The selection of a catalyst for instance, is determined in the first place by the requirements imposed by any future user of the liquid product. Such requirements could be assigned according to targeting on *e.g.* the degree of deoxygenation and/or the production of target chemical compounds in high yields. In order to obtain target products in CFP of biomass with desired yields and compositions, the influence of the *reactor type*, the *operation mode* (*e.g.* in situ, ex situ), and *the type and the performance of a catalyst* (*e.g.* resistance to deactivation) in the specified process conditions should be well defined.

Reactors

In this study, we used two types of continuously operated (catalytic) fast pyrolysis reactors, *viz.* an auger reactor and a mechanically stirred bed reactor. Both setups were validated by performing several non-catalytic and catalytic experiments.

The first part of the experimental work (discussed in Chapters 3 & 4) was concerned with the operation and the validation of a fully controlled mini-plant (0.5 kg/h intake) based on auger reactor technology. This mini-plant was designed to allow three types of biomass fast pyrolysis experiments, *viz.* non-catalytic, in situ catalytic fast pyrolysis, and ex situ upgrading of non-catalytic fast pyrolysis vapours by means of a downstream, moving-bed catalytic reactor. It allows a stable operation under a wide range of process conditions to maintain high mass balance closures and good reproducibility of the experiments. The product yields obtained were in-line with literature data for lignocellulosic biomass fast pyrolysis.

The second part of the experimental work (discussed in Chapters 5 & 6) was concerned with the design, construction, and operation of a fully controlled, continuously operating lab-scale pyrolysis set-up (0.2 kg/h intake). This set-up was designed to allow non-catalytic and in situ catalytic pyrolysis experiments. The unique feature of this reactor is that it contains a specially designed mixer (ribbon type) that ensures a uniform mixing of the bed contents (catalyst and sand) without any segregation. Hence, the inert gas flow could be reduced (lower than the minimum fluidization velocity, U_{mf}) which in turn improves the condensation.

The operation mode

Based on the location of the catalyst in the process, CFP of biomass can be performed in two different operation modes, *viz.* in situ and ex situ. In the in situ mode, the CFP occurs in a single reactor (*i.e.* in situ reactor) where the biomass feedstock and the catalyst are physically mixed to enable a good contact between the two. The primary fast pyrolysis vapours, released after the thermal decomposition of biomass particles, are reformed by the catalysts during their mutual contact time. In the ex situ mode on the other hand, the primary pyrolysis vapours produced inside the first reactor (*i.e.* non-catalytic pyrolysis reactor) are transferred to a secondary reactor (*i.e.* ex situ reactor) where they are contacted with –and thus reformed by– the catalyst.

To test the effect of the operation mode on the product yields and compositions of CFP of biomass, we performed in- and ex situ catalytic fast pyrolysis of pine wood in an auger reactor with a single type of heterogeneous ZSM-5 based acidic catalyst while the non-catalytic results were taken as reference. The reaction temperature and the catalyst-to-biomass ratios were kept constant at 500 °C and 5, respectively both for in- and ex situ operation modes. The application of the catalyst resulted in a significant decrease in the overall liquid yields; they decreased from 58.9 wt.%* (the reference non-catalytic case) to 50.3 wt.% and 50.1 wt.%, for in- and ex situ respectively. The yields of organic fractions of liquids in both cases were similar (*ca.* 17 wt.%) and lower than that obtained from non-catalytic fast pyrolysis (37 wt.%). For ex situ CFP of biomass, the decrease of char yield was marginal (0.2 wt.%) compared to the non-catalytic fast pyrolysis. However, a significant decrease (2.3 wt.%) of char yield was observed for the in situ mode; this was ascribed to the higher mass ratio of heat carrier-to-biomass that results in a higher conversion (devolatilization) of biomass particles into vapours. In situ CFP led to a higher yield in gas products than ex situ CFP (26.2 wt.% vs. 23.9 wt.%), while the ex situ CFP led to a slightly higher coke deposition on the catalyst (7.5 wt.% vs. 7.1 wt.%). Both in situ and ex situ CFP led to effective oxygen removal and the conversion of high-molecular weight compounds to lower ones. The use of in- and ex situ catalysis resulted in a removal of detectable sugars and aldehydes. In both cases, the concentration of organic acids was decreased while in situ CFP resulted in much higher selectivity to phenols and aromatic hydrocarbons than that of ex situ CFP. Moreover, compared with the in situ mode, ex situ mode consumed less catalyst (more than a factor of 2) to reach the same catalyst-to-biomass ratios due to the variations in the catalyst feed rates. However, the overall performance of in situ catalysis in terms of oil quality was considerably better. Future research could focus on testing the effect of the operation modes on the product yields and compositions of CFP of biomass with respect to different reactor temperatures, catalysts, and catalyst-to-biomass ratios.

* All yields were reported based on biomass weight (as received).

Evaluation of the performance of various catalysts

We performed the screening of metal doped heterogeneous catalysts (and their metal doped counterparts) in in situ catalytic fast pyrolysis of pine wood. The experiments were performed in a continuously operated auger reactor at 500 °C. This work was meant to assess the efficiency of various catalysts in terms of their capability to deoxygenate the pyrolysis vapours, and observe their potential to produce a liquid mixture that could be used as a renewable feedstock in petrochemical industries. In total, eight proprietary catalysts were tested. They were divided into three groups based on their acidity, type of carrier, the active metal they contain, and according to being aged or fresh. The results obtained from catalytic tests have been compared to each other and to non-catalytic control experiments performed with sand. The main objective was to find the best performing catalysts capable of retaining the amount of the organic liquid products as much as possible with a minimum water production, and also achieving an effective reduction of the acidity during in situ catalytic fast pyrolysis of pine wood.

The presence of catalysts led to the production of additional water, coke and gases at the expense of the liquid organics and char. However, the quality of the obtained liquid products was altered in various ways depending on the catalyst type and its active metal content; HHV of the organic phase increased in the range of 18 % to 57 % while the total acid number (TAN) obtained from sand experiments decreased from 103 down to values ranging between 77 and 4. For all catalysts, the acidity of CFP-oils remarkably decreased with an increased deoxygenation. In order to determine the performances of the catalysts tested under identical process conditions, two separate evaluations were made based on various defined criteria. The considered criteria were the deoxygenation by CO₂ (the preferred route for deoxygenation), the yield of organic liquid phase, H/C ratio of the organic liquid phase, O/C ratio of the organic liquid phase, coke yield, the production of desirable compounds, energy content in the organic liquid phase, and the percentage of the detectable components in the organics.

It is important to notice that the market for the products of CFP of biomass is not clearly specified and the definition of product specifications are lacking at this stage of the technology development. Hence, although subjective and depending on the target application, the order of the weight factors was determined based either on the deoxygenation requirements or on the production of desirable compounds in high yields (Tables A.4.2.1a & A.4.2.1b in Appendix 4.2). Among all catalysts, the acidic catalyst containing some redox active metal, the basic catalyst with a mixture of two metal oxides (calcined), and a metal oxide doped gamma-alumina catalyst (calcined) were found to be the best performing ones. The catalysts were also tested on a micro-scale using a py-GC/MS system. The py-GC/MS results were found to be only partially indicative for the performance of a catalyst in CFP. An optimally configured py-GC/MS can be used as a rapid screening tool prior to the time consuming larger scale CFP experiments only if the py-GC/MS is quantitatively calibrated for a number of well-defined specific compounds of interest. For the exact determination of the deoxygenation performance as well as to assess the complete composition and quality of the bio-oil, larger scale catalytic experiments are indispensable.

Lifetime and deactivation of a catalyst

One of the problems in CFP of biomass, hardly discussed in the literature, is the rate and extent of catalyst deactivation that affects the lifetime of the catalyst negatively. Deactivation implies the physical, chemical, thermal, and mechanical degradation of the catalyst leading to a reduced activity and selectivity. Various mechanisms causing catalyst deactivation are known, such as fouling, poisoning, attrition, and dealumination. In catalytic fast pyrolysis of biomass, deactivation can be mainly attributed to coke deposition, which blocks the pores and thus the active sites of zeolites. Some degree of deactivation by deposition of contaminants (alkali and alkali earth metals; AAEM's) originally present in the biomass cannot be excluded either (poisoning).

Like in conventional FCC (fluid catalytic cracking) processing of petroleum oil, the catalysts deactivated by coke can be reused in a CFP process after being regenerated. In FCC regeneration, the catalyst is subjected to high temperature oxidative treatment to burn the coke off from the catalyst and thereby (partially) restore its activity. In biomass CFP however, the coke-on-catalyst contains some oxygen and hydrogen. Regeneration of the catalysts thus

yields water, apart from only CO_x ($\text{CO} + \text{CO}_2$), which for ZSM-5 and similar structured catalysts could lead to dealumination, and thus loss of active (acid) sites. We investigated the effect of a repeatedly regenerated ZSM-5-based catalyst (eight reaction/regeneration cycles in total) on the yields and compositions of the pyrolysis products in relation to the applied process conditions and on the catalyst itself. Experiments were performed at 500 °C in a mechanically stirred sand bed reactor using pine wood as the biomass feedstock. Along the reaction/regeneration sequence, the yield of organics increased, while water, carbonaceous solids, and non-condensable gases decreased. Trends in pyrolysis product yields converging to that of non-catalytic levels were observed, which revealed that the activity, and thus the influence of the catalyst slowly declined. The main observation was that the catalyst partially loses its activity (BET surface area reduced by 63 %) in terms of the product distribution along the reaction/regeneration sequence, while retaining sufficient activity in producing the target chemical compounds (*e.g.* aromatics). New catalyst formulations, vapour phase treatment (*ex situ* CFP) instead of *in situ* catalysis, improved catalyst regeneration procedures, application of other temperatures, and optimization of space velocities are all possible strategies to further improve the result of the catalytic fast pyrolysis process.

Through successive cycles of pyrolysis and catalyst regeneration, a considerable amount of biomass originated mineral matter (in the form of ash) accumulates in the CFP process. This could potentially affect the chemistry of the catalytic pyrolysis as well as the stability and/or the activity of the catalyst. To understand the role of indigenous and added inorganic compounds in CFP of biomass, and the potential ash/catalyst interactions that may take place in CFP, we investigated the influence of them on the distribution and composition of products resulting from the primary and secondary fast pyrolysis reactions. The effects of the pine wood ash were studied by comparing non-catalytic and catalytic experiments (using a ZSM-5 based catalyst) with their ash-added counterparts. To show the case of ash accumulated from the biomass feeding, the results of catalytic fast pyrolysis obtained after eight reaction/catalyst regeneration cycles were included as well. Ash concentrations as low as *ca.* 3 wt.% relative to the amount of pine wood fed, and *ca.* 0.002 wt.% relative to the amount of bed material, were found sufficient to have a direct effect on the yield and composition of the CFP products. To overcome the drawbacks of biomass ash in CFP, the char (which contains a vast majority of the biomass ash) has to be physically removed from the catalyst before the regeneration step. The biomass feedstock used in this study (pine wood) is a low-ash feedstock. With the use of high-ash containing feedstock, and the larger number of reaction/regeneration cycles desired in future large scale installations, the effect of ash will be even more dramatic. Future research should reveal whether the observed trends will persist after many more reaction/regeneration cycles, and how long it takes for the catalyst to completely deactivate. Strategies to reduce the mineral burden in the CFP process could extend the lifetime of the catalyst.

Additional remarks

Most of the literature studies concerning CFP of biomass deal with the catalyst screening in small laboratory systems. However, the efficient and the economical use of all the products of the process, and the operational barriers related to the implementation of CFP technology at a large scale, are hardly discussed. This thesis, therefore, focussed on various aspects of continuous operation.

In CFP of biomass, the main problem to be dealt with is the presence of the biomass originated alkaline ash which destroys and physically swamps any catalyst utilized in the process. Practically, the direct physical contact between the catalyst and the biomass must be prevented in order to achieve a successful operation. Hence, prior to scaling up this technology to a commercial level, this particular problem should be clearly identified and solved. A solution may be to separate the biomass fast pyrolysis from the catalytic treatment of the vapours (*i.e.* ex situ processing mode). Although technically challenging and costly, ex situ operation provides some more flexibility in selecting the optimal conditions for catalysis. In this way, the periodic regeneration of the spent catalysts by coke combustion can be conducted in the absence of char which contains the vast majority of the biomass ash. Hence, the physical contact between the biomass minerals and the catalyst is excluded (no risk of catalyst poisoning by minerals) so that the activity of the catalyst is eventually conserved over a much longer period. This allows the catalyst to be re-used for larger number of reaction/regeneration cycles than that of in an in situ operation. However, the quality and quantity of the CFP-products obtained in the ex situ processing may be different from those of in situ processing. The reason for this difference could be that the catalyst is not contacted directly with the primary fast pyrolysis vapours, but with the vapours that may have changed their composition during the transfer from the pyrolysis reactor to the catalytic reactor. This must be investigated more thoroughly.

In general, five major factors influence the CFP process:

- the type and the properties of the biomass feedstock,
- the process parameters (*i.e.* temperature, heating rate, catalyst-to-feed ratio, vapour residence time, *etc.*),
- the choice of the reactor technology,
- the operation mode (*i.e.* in- or ex situ),
- and the type of the catalyst used.

The success of the process is closely related to the precise optimization of these factors which would yield a maximum quantity of catalytic fast pyrolysis oil (CFP-oil) of a certain quality, while minimizing the amounts of by-products (*i.e.* char, coke on catalyst, and non-condensable gases). Based on these constraints, the catalyst design should focus on the production of cheap catalysts with improved abilities for cracking, deoxygenation, and the resistance to deactivation. Keeping in mind that the catalyst screening in small scale laboratory setups (*e.g.* pyroprobes, *mg*-scale batch reactors) is not the ultimate target but a tool for the development of this technology, the best performing catalysts in such studies should be tested in larger scale continuous setups allowing longer operations. For that

purpose, the importance should be given to the design of novel catalytic systems and new reactor technologies, based on the specific process requirements for catalytic fast pyrolysis rather than that of conventional fast pyrolysis.

Supporting Information

Table A.2.1. Literature publications regarding the in situ catalytic fast pyrolysis of lignocellulosic biomass (published between 1988 – March 2014) with respect to the reactor type and feedstock type. The reason for overlapping numbers is due to more than one type of reactor or feedstock type was studied in some publications.

Operation mode	No. of appearance in publications	Reactor type	No. of appearance in publications	Feedstock type	No. of appearance in publications
In situ ^a	76	Fluidized bed ^b	24	Woody biomass	20
				Residual biomass ^d	4
				Lignin	-
				Cellulose	-
				Hemicellulose	-
				Other feedstock ^e	-
		Fixed bed	16	Woody biomass	4
				Residual biomass ^d	5
				Lignin	-
				Cellulose	-
				Hemicellulose	-
				Other feedstock ^e	9
		py-GC/MS, pyroprobes and benchtop pyrolyzers	22	Woody biomass	11
				Residual biomass ^d	6
				Lignin	6
				Cellulose	6
				Hemicellulose	1
				Other feedstock ^e	8
		Others ^c	21	Woody biomass	10
				Residual biomass ^d	7
				Lignin	2
				Cellulose	-
				Hemicellulose	-
				Other feedstock ^e	4

^a Biomass and the catalyst are physically mixed in the reactor.

^b Includes bubbling and circulating fluidized beds.

^c Reactor types are: Wire mesh captive sample reactor, static bed catalytic reactor, conical spouted bed reactor, micro-activity test reactor, TGA, TGA/MS, FTIR, quartz (tube) reactor, auger reactor, stainless steel tube, microwave oven, Curie-point pyrolyzer, down flow quartz reactor.

^d Agricultural residues and industrial by-products, including husks, cobs, stovers, peels, stalks, straws, seeds, grain, bagasse and non-woody biomasses such as miscanthus, switchgrass, jatropha and cassava rhizome.

^e Other feedstock include some model compounds such as glucose, furan, furfural, levoglucosan, methanol, furfural, glycerol, sorbitol, xylitol, cellobiose, etc.

Table A.2.2. Literature publications regarding the ex situ catalytic fast pyrolysis of lignocellulosic biomass (published between 1988 – March 2014) with respect to the reactor type and feedstock type. The reason for overlapping numbers is due to more than one type of reactor or feedstock type was studied in some publications.

Operation mode	No. of appearance in publications	Reactor type	No. of appearance in publications	Feedstock type	No. of appearance in publications
Ex situ ^a	54	Fluidized bed combined with a fixed catalyst bed	9	Woody biomass	8
				Residual biomass ^d	1
				Lignin	-
				Cellulose	-
				Hemicellulose	-
				Other feedstock ^e	-
		Tubular fixed bed ^b	14	Woody biomass	9
				Residual biomass ^d	4
				Lignin	-
				Cellulose	-
				Hemicellulose	-
				Other feedstock ^e	1
		py-GC/MS, pyroprobes and benchtop pyrolyzers combined with a fixed catalyst bed	20	Woody biomass	8
				Residual biomass ^d	8
				Lignin	6
				Cellulose	3
				Hemicellulose	2
				Other feedstock ^e	-
		Others - combined with a fixed catalyst bed ^c	12	Woody biomass	7
				Residual biomass ^d	3
				Lignin	3
				Cellulose	2
				Hemicellulose	-
				Other feedstock ^e	1

^a Produced non-catalytic pyrolysis vapours flow through a fixed or moving catalyst bed.

^b Biomass and catalyst are separated with a quartz wool in the same tubular fixed bed reactor.

^c Reactor types are: Vortex reactor, quartz micro reactor, TG/MS, TGA, quartz (tube) reactor, stainless steel tube reactor.

^d Agricultural residues and industrial by-products, including husks, cobs, stovers, peels, stalks, straws, seeds, grain, bagasse and non-woody biomasses such as miscanthus, switchgrass, jatropha and cassava rhizome.

^e Other feedstock are some model compounds such as: glucose, furan, furfural, levoglucosan, methanol, furfural, glycerol, sorbitol, xylitol, cellobiose, *etc.*

Table A.2.3. *In situ* catalytic pyrolysis studies based on the utilization of microporous zeolites using various types of woody biomasses as feedstock. Reactor types and process conditions are provided.

Entry	Catalyst (Si/Al ratio)	Feedstock	Reactor	T (°C)	Catalyst-to-feed ratio (w/w)	WHSV (h ⁻¹)	Vapour residence time (s)	Heating rate	Ref./ Year
1	H-ZSM-5	Hybrid poplar wood	Fluidized-bed	450	-	2	1-2	-	[101] 2010
2	H-ZSM-5	Hybrid poplar wood	Fluidized-bed	500	-	0.5	1	-	[76] 2010
3	FCC (2.67), P-ZSM-5 (3.03), ZSM-5 (7.78)	Hybrid poplar wood	Fluidized-bed	475	-	2	3 and 6.5	-	[102] 2012
4	FCC, FCC/FeCrCu, FCC/CoMo, FCC/FeCrCu/CoMo	Hybrid poplar wood	Fluidized-bed	475	-	2	3 and 6.5	-	[156] 2012
5	FCC	Hybrid poplar wood	Fluidized-bed	400, 500, 600	-	1, 2, 3	3, 4.5 and 6	-	[82] 2013
6	Fresh Y-zeolite FCC, steamed Y-zeolite FCC, fresh ZSM-5 additive, steamed ZSM-5 additive	Hybrid poplar wood	Fluidized-bed	475	-	2	6	-	[103] 2014
7	H-Beta (25), H-Beta (150), H-Beta (300)	Pine wood	Fluidized-bed	450	-	1.25	-	-	[125] 2007
8	H-Beta (25), H-Y (12), H-ZSM-5 (23), H-MOR (20)	Pine wood	Fluidized-bed	450	-	1.67	5.9	-	[104] 2008

Table A.2.3. continued

Entry	Catalyst (Si/Al ratio)	Feedstock	Reactor	T (°C)	Catalyst-to- feed ratio (w/w)	WHSV (h ⁻¹)	Vapour residence time (s)	Heating rate	Ref./ Year
9	FCC, ZSM-5 based FCC (10 wt. % USY)	Lignocel HBS 150- 500 (beech wood originated)	Fluidized- bed*	400-500	Solid material/biomass ratio: 3.5 and 22 for FCC; 2.9, 4.3 and 18 for ZSM-5 based FCC	-	<1	-	[32] 2002
10	FCC	Beech wood	Fluidized- bed*	450, 500	16	-	-	-	[64] 2009
11	ZSM-5 (30)	Pine wood	Fluidized-bed	600, 675	-	0.1, 0.2, 0.8, 1.7	26 (gas res.time)	-	[92] 2011
12	ZSM-5 (15), silylated ZSM-5 (15), Ga-ZSM-5 (15), silylated Ga-ZSM-5 (15)	Pine wood	Fluidized-bed	550	-	0.38, 0.39, 0.47	-	-	[157] 2012
13	ZSM-5 (30), Ga/ZSM-5 (30)	Pine wood	Fluidized-bed	550, 600	-	0.35	-	-	[127] 2012
14	ZSM-5	Pine wood	Fluidized-bed	400, 450, 500, 600, 650	-	0.11, 0.18, 0.35, 0.60, 0.97, 1.98 (at 600 °C)	-	-	[105] 2012
15	ZSM-5	Pine wood	Fluidized- bed*	600	3, 4.5, 6, 9 (at 0.3 wood WHSV)	0.15, 0.3, 0.6, 0.9 (at cat./biomass ratio of 6)	1.36	-	[98] 2014
16	ZSM-5	Mixed wood	Fluidized-bed	500	-	0.48	0.7	-	[106] 2013
17	ZSM-5 (11.5), ZSM-5 (25), ZSM-5 (140)	European spruce	Fluidized-bed	500	-	2.3, 3.1 and 4.3	0.8	-	[86] 2013

Table A.2.3. continued

Entry	Catalyst (Si/Al ratio)	Feedstock	Reactor	T (°C)	Catalyst-to- feed ratio (w/w)	WHSV (h ⁻¹)	Vapour residence time (s)	Heating rate	Ref./ Year
18	H-ZSM-5 (28)	Pine-spruce mixture	Fluidized-bed	450	-	-	-	-	[158] 2014
19	ZSM-5 (30)	Pine wood	Py-GC/MS	600	19	-	-	1000 °C/s for filament	[92] 2011
20	H-ZSM-5 (50)	Pine wood	Py-GC/MS	550	4 and 9	-	-	50 °C/s for biomass, 2000 °C/s for filament	[52] 2011
21	Low, moderate and high acid catalysts, dealuminated- zeolite Y, β -zeolite, mordenite	Oak sawdust	Py-GC/MS	600	10	-	-	30 °C/s for biomass, 2000 °C/s for filament	[57] 2011
22	ZSM-5 (30) and tartaric acid treated ZSM-5	Maple wood	Py-GC/MS	600	19	-	-	1000 °C/s for filament	[70] 2012
23	H-ZSM-5 (28), H- ZSM-5 (80), SN27 (24-27), MSN-15 (13-15), MSM-15 (13-15)	Beech wood	Py-GC/MS	500	0.1 and 0.4 (for MSM-15 and H- ZSM-5 (80) only)	-	-	-	[159] 2011
24	H-USY (10), H-Beta (40), H-Mordenite (18), H-ZSM-5 (23)	Cedar wood	Py-GC/MS	500	1 and 5	-	-	-	[41] 2013
25	H-ZSM-5 (25) with different mean crystal sizes (2 μ m, 200 nm and 50 nm)	Pine wood	Py-GC/MS	600	9	-	50	20000 K/s	[160] 2014
26	ZSM-5 (25.5)	Beech wood	Py-GC/MS	650	10	-	-	2000 °C/s for filament	[161] 2014

Table A.2.3. continued

Entry	Catalyst (Si/Al ratio)	Feedstock	Reactor	T (°C)	Catalyst-to- feed ratio (w/w)	WHSV (h ⁻¹)	Vapour residence time (s)	Heating rate	Ref./ Year
27	H-ZSM-5 (50), Co(5 wt. %)/HZSM- 5 (50), Ni(5 wt. %)/HZSM-5 (50), Mo(5 wt. %)/HZSM-5 (50), Pt(5 wt. %)/HZSM-5 (50)	Pine wood	Py-GC/MS	650	9	-	-	2000 °C/s for filament	[162] 2012
28	H-ZSM-5 (150), H- Mordenite	Pine wood	Py-GC-MIP- AED	500	1	-	-	-	[110] 2010
29	H-ZSM-5	Lignocel HBS 150- 500 (beech wood originated)	Packed-bed	500	~0.5	-	-	-	[69] 2000
30	Low, moderate and high acid catalysts, dealuminated-zeolite Y, β -zeolite, mordenite	Oak sawdust	Packed-bed	600	5	-	-	-	[57] 2011
31	Re-USY (1.35), ZSM-5 (24)	Pine bark	Packed-bed	300, 400, 500, 600	0.05	-	-	7 °C/min	[163] 2012
32	Three types of faujasite based FCC catalysts: Na-FAU, Na _{0.2} H _{0.8} -FAU, H- FAU	Pine wood (Canadian white)	Packed-bed	500	0.1	-	4	40 °C/s	[164] 2013
33	ZSM-5 based FCC	Pine wood	Auger screw*	500	5	-	ca. 1	-	[100] 2013
34	H-ZSM-5 (24)	Pine wood	Conical spouted-bed	400, 450, 500	-	-	0.5	-	[99] 2000

Table A.2.3. continued

Entry	Catalyst (Si/Al ratio)	Feedstock	Reactor	T (°C)	Catalyst-to- feed ratio (w/w)	WHSV (h ⁻¹)	Vapour residence time (s)	Heating rate	Ref./ Year
35	H-ZSM-5 (24)	Pine wood	Conical spouted-bed	400	2, 5, 13	-	0.5	-	[124] 2005
36	ZSM-5 (50)	Douglas fir	Batch microwave oven	400, 500, 600	1.32, 2, 3, 4, 4.68	-	-	100 °C/min	[165] 2012

* Continuous processes

Table A.2.4. *Ex situ* catalytic pyrolysis studies based on the utilization of microporous zeolites using various types of woody biomasses as feedstock. Reactor types and process conditions are provided.

Entry	Catalyst (Si/Al ratio)	Feedstock	Pyrolysis reactor (T, °C)	Ex situ catalytic reactor (T, °C)	Catalyst-to-feed ratio (w/w)	WHSV (h ⁻¹)	Vapour residence time (s)	Heating rate	Ref./Year
1	H-Fer (20), Fe-H-Fer (20), H-Y (12), Fe-H-Y (12), H-β (25), Fe-H-β (25)	Pine wood	Fluidized-bed (400)	Fluidized-bed (450)	0.11	-	-	-	[132] 2010
2	ZSM-5	Wood mixture	Fluidized-bed (550)	Fluidized-bed (400, 450, 500, 550)	-	1.05-1.14	0.4	-	[107] 1994
3	ZSM-5	Wood mixture	Fluidized-bed (550)	Packed bed (400, 450, 500, 550)	-	-	-	-	[129] 1944
4	ZSM-5 (50)	Wood mixture	Fluidized-bed (550)	Fluidized-bed (500)	1.16	1	-	-	[108] 1995
5	ZSM-5	Wood mixture	Fluidized-bed (550)	Packed bed (500)	-	~2	0.2 to 0.8	-	[128] 1996
6	H-ZSM-5 (50)	Sawdust	Fluidized-bed (500)	Packed bed (390, 410, 450, 470, 550)	-	1 to 5	-	-	[51] 2008
7	H-ZSM-5 (26), H-Y (4), Ga/H-ZSM-5, Ga/H-Y	Radiata pine	Fluidized-bed (475)	Packed bed (450~550)	0.1 and 0.2	-	-	-	[130] 2007
8	ZSM-5 (25)	Radiata pine	Fluidized-bed (475)	Packed bed (450~550)	0.1 and 0.2	-	-	-	[130] 2008
9	H-ZSM-5 (50)	Pine wood	Pyroprobe (550)	Packed bed (550)	2 and 5	-	-	50 °C/s for biomass, 2000 °C/s for filament	[52] 2011

Table A.2.4. continued

Entry	Catalyst (Si/Al ratio)	Feedstock	Pyrolysis reactor (T, °C)	Ex situ catalytic reactor (T, °C)	Catalyst-to-feed ratio (w/w)	WHSV (h ⁻¹)	Vapour residence time (s)	Heating rate	Ref./Year
10	H-Mordenite (20), H-ZSM-5 (23, 50, 280), H-Y (5.1), H-Beta (23, 38, 360), H-Ferrierite (20)	Oak wood	Micro pyrolyzer (550)	Packed bed (550)	5	-	-	-	[109] 2011
11	Re-USY (1.35), ZSM-5 (24)	Pine bark	Packed-bed (300, 400, 500, 600)	Packed-bed (400)	0.05	-	-	7 °C/min	[163] 2012
12	H-ZSM-5 (20.1)	Radiata pine	Packed-bed (500)	Packed-bed (500)	0.1	-	5 (in the pyrolysis reactor)	-	[138] 2010
13	ZSM-5	Softwood	Packed-bed (510)	Packed-bed (400)	-	-	1.5 (in the transfer line)	-	[166] 1988
14	Three types of faujasite based FCC catalysts: Na-FAU, Na _{0.2} H _{0.8} -FAU, H-FAU	Pine wood (Canadian white)	Packed-bed (500)	Packed-bed (500)	0.1	-	4	40 °C/s	[164] 2013
15	H-ZSM-5	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed-bed (500)	~0.5	-	-	-	[69] 2000
16	ZSM-5 (138), ZSM-5 (90), ZSM-5 (61), FCC	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed-bed (500)	~0.5	-	0.031 (for FCC)	-	[147] 2011
17	ZSM-5 (25)	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed-bed (500)	~0.5	-	<0.1	-	[167] 2011

Table A.2.4. continued

Entry	Catalyst (Si/Al ratio)	Feedstock	Pyrolysis reactor (T, °C)	Ex situ catalytic reactor (T, °C)	Catalyst-to-feed ratio (w/w)	WHSV (h ⁻¹)	Vapour residence time (s)	Heating rate	Ref./Year
18	ZSM-5 (80), Ni(1%)/ZSM-5, Ni(5%)/ZSM-5, Ni(10%)/ZSM-5, Co(1%)/ZSM-5, Co(5%)/ZSM-5, Co(10%)/ZSM-5	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed-bed (500)	~0.5	-	<0.1	-	[131] 2012
19	ZSM-5, Y and SAPO type zeolites, metal modified ZSM-5 (for a complete list of catalysts, see the publication)	Aspen wood	Tubular quartz micro reactor (600)	Tubular quartz micro reactor (600)	-	4	-	-	[59] 2010
20	ZSM-5 based FCC	Pine wood	Auger screw (500)*	Moving bed, co- current contact (500)*	5	-	3	-	[100] 2013

* Continuous processes

Table A.2.5. *In- and ex situ* catalytic pyrolysis studies based on the utilization of mesoporous catalysts using various types of woody biomasses as feedstock. Reactor types and process conditions are provided.

Entry	Catalyst (Si/Al ratio)	Feedstock	Pyrolysis (in situ) reactor (T, °C)	Ex situ catalytic reactor (T, °C)	Catalyst-to-feed ratio (w/w)	Vapour residence time (s)	Heating rate	Ref./Year
1	Meso-ZSM-5 and tartaric acid treated Meso-ZSM-5	Maple wood	Semi-batch pyroprobe (600)	-	19	-	1000 °C/s for filament	[70] 2012
2	Desilicated Meso-ZSM-5: ZSM-5-0.1M (25.5), ZSM-5-0.2M (25.0), ZSM-5-0.3M (24.0), ZSM-5-0.4M (21.6), ZSM-5-0.5M (21.1)	Beech wood	Semi-batch pyroprobe (650)	-	10	-	2000 °C/s for filament	[161] 2014
3	Al-MCM-41 (parent and calcined)	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	-	~0.5	-	-	[69] 2000
4	Mesoporous aluminosilicate molecular sieve	Oak sawdust	Packed-bed (600)	-	5	-	-	[57] 2011
5	Al, Sn, Fe, Mo, Co, Ti, Zr impregnated on MCM-41	Pine wood	Py-GC-MIP-AED (500)	-	1	-	-	[110] 2010
6	Meso-Beta (13.6), Meso-ZSM-5 (20.1), Al-MCM-41	Radiata pine	Fluidized-bed (475)	Packed bed (450~550)	0.1 and 0.2	-	-	[137] 2008
7	Al-MCM-41 (20), MCM-41 with spacer, MCM-41 with C ₁₈ , Cu-Al-MCM-41	Spruce wood	Pyroprobe (450, 500)	Packed-bed (450, 500)	1	-	-	[136] 2005
8	SBA-15, Al-SBA-15 (10), Al-SBA-15 (20), Al-SBA-15 (35), Al-SBA-15 (70)	Fir wood	Pyroprobe (500)	Packed-bed (500)	1	-	2000 °C/s for filament	[139] 2009
9	Al-MCM-41 (20), MCM-41 with spacer, MCM-41 with C ₁₈ , Cu-Al-MCM-41, SBA-15, Al-SBA-15, FCC	Spruce wood	Packed-bed (500)	Packed bed (500)	~0.5	~4.5	-	[168] 2006

Table A.2.5. continued

Entry	Catalyst (Si/Al ratio)	Feedstock	Pyrolysis (in situ) reactor (T, °C)	Ex situ catalytic reactor (T, °C)	Catalyst-to-feed ratio (w/w)	Vapour residence time (s)	Heating rate	Ref./Year
10	Meso-ZSM-5 (18.2), Meso-MFI, 1 wt.% Ga/Meso-MFI, 5 wt.% Ga/Meso-MFI	Radiata pine	Packed-bed (500)	Packed-bed (500)	0.1	5 (in the pyrolysis reactor)	-	[138] 2010
11	Al-MCM-41 (20), Al-MCM-41 (40), Al-MCM-41 (60), Cu-Al-MCM-41, Fe-Al-MCM-41, Zn-Al-MCM-41	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed bed (500)	~0.5	~4.5	-	[135] 2006
12	Al-MCM-41 (parent and calcined)	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed-bed (500)	~0.5	-	-	[69] 2000
13	MSU-S/H _{BEA} , MSU-S/W _{BEA} , Al-MCM-41	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed bed (500)	~0.5	~4.5	-	[169] 2007
14	MCM-41, Al-MCM-41 (30), Al-MCM-41 (50), Al-MCM-41 (30)-steamed at 550 °C, Al-MCM-41 (50)-steamed at 750 °C,	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed bed (500)	~0.5	~4.5	-	[133] 2007
15	Al-MCM-41 (30)	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed-bed (500)	~0.5	<0.1	-	[167] 2011

Table A.2.6. *In- and ex situ* catalytic pyrolysis studies based on the utilization of basic (metal oxides) and metal catalysts using various types of woody biomasses as feedstock. Reactor types and process conditions are provided.

Entry	Catalyst (Si/Al ratio)	Feedstock	Pyrolysis (in situ) reactor (T, °C)	Ex situ catalytic reactor (T, °C)	Catalyst-to-feed ratio (w/w)	Vapour residence time (s)	Heating rate	Ref./Year
Basic catalysts (metal oxides):								
1	NiMo/Al ₂ O ₃ , CoMo/Al ₂ O ₃ , CoMo-S/Al ₂ O ₃ , Al ₂ O ₃ , SiO ₂ , P-SiO ₂ (porous)	Pine wood, spruce wood (Alaskan), lauan wood (tropical)	Fluidized-bed (500, 600, 700, 800, 900)	-	-	-	-	[146] 2008
2	Co/Al ₂ O ₃ , Co/SiO ₂ , ZrO ₂ , SnO ₂ , CaO, ZnO, Fe ₂ O ₃ , CuO, MoO ₃ , TiO ₂ , WO ₃ , MgO, Cu-ZnO-ZrO ₂ /Al ₂ O ₃ , Fe-Zn-Cu/Al ₂ O ₃ , Fe-Cu-Al-Zn/Al ₂ O ₃ , Co/ZrO ₂ , Cu/ZrO ₂	Pine wood	Py-GC-MIP-AED (500)	-	1	-	-	[110] 2010
3	K ₃ PO ₄	Poplar wood, pine wood	Pyroprobe (300-600)	-	~1	-	2000 °C/s for filament	[170] 2013
4	Naturally occurring metal hydroxide containing mineral	Oak sawdust	Pyroprobe (600)	-	10	-	30 °C/s for biomass, 2000 °C/s for filament	[57] 2011
5	Naturally occurring metal hydroxide containing mineral	Oak sawdust	Packed-bed (600)	-	5	-	-	[57] 2011
6	CaO, FeO, Al ₂ O ₃ , MnO, Cr ₂ O ₃ , CuO	Sawdust	Batch pyrolysis apparatus (500)	-	0.1, 0.2, 0.3, 0.4, 0.5	-	-	[171] 2003
7	NaOH, Na ₂ CO ₃ , Na ₂ SiO ₃ , NaCl, TiO ₂ , H ₃ PO ₄ , Fe(SO ₄) ₃	Pine wood	Microwave (470)	-	0.1	-	-	[172] 2008
8	ZnO (0.5% Mg), SiC	Pine sawdust	Fluidized-bed (525)	Packed bed (400)	-	0.15	-	[142] 2000
9	ZnO, ZnO (0.5% Mg), ZnO (15% alumina)	Pine sawdust	Pyroprobe (600)	Packed bed (600)	-	0.03	-	[142] 2000

Table A.2.6. continued

Entry	Catalyst (Si/Al ratio)	Feedstock	Pyrolysis (in situ) reactor (T, °C)	Ex situ catalytic reactor (T, °C)	Catalyst-to-feed ratio (w/w)	Vapour residence time (s)	Heating rate	Ref./Year
10	TiO ₂ (rutile), TiO ₂ (anatase) and ZrO ₂ /TiO ₂ (a mix. of 40 wt.% TiO ₂ (anatase) and 60 wt.% ZrO ₂)	Poplar wood	Pyroprobe (500)	Packed-bed (500)	2	-	2000 °C/s for filament	[145] 2010
11	MgO, CaO, TiO ₂ , Fe ₂ O ₃ , NiO, ZnO	Poplar wood	Pyroprobe (500)	Packed-bed (500)	1	-	2000 °C/s for filament	[144] 2010
12	Red mud (a mixture of Fe ₂ O ₃ , Al ₂ O ₃ , SiO ₂ , TiO ₂ , Na ₂ O, CaO)	Pine bark	Packed-bed (300, 400, 500, 600)	Packed-bed (400)	0.05	-	7 °C/min	[163] 2012
13	MgO, NiO	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed-bed (500)	~0.5	<1	-	[147] 2011
14	CoO, Co ₃ O ₄ , NiO	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed-bed (500)	~0.5	<0.1	-	[131] 2012
Metal catalysts:								
15	A metal based catalyst with Ni/Al ratio of 0.5	Pine wood	Fluidized-bed (650, 700)	-	0.2	0.34	-	[173] 2001
16	Fe/Cr	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	-	~0.5	-	-	[69] 2000
17	Ni and Fe (impregnated on biomass)	Oak wood	Tubular heated (700)	-	-	-	-	[174] 2007
18	ZnCl ₂	Fir wood	Downflow quartz reactor (lab scale) (250-500)	-	-	-	-	[175] 2011
19	ZnCl ₂ (impregnated on biomass)	Poplar wood	Pyroprobe (350, 400, 500, 600)	-	0.05	-	2000 °C/s for filament	[176] 2011

Table A.2.6. continued

Entry	Catalyst (Si/Al ratio)	Feedstock	Pyrolysis (in situ) reactor (T, °C)	Ex situ catalytic reactor (T, °C)	Catalyst-to-feed ratio (w/w)	Vapour residence time (s)	Heating rate	Ref./Year
20	ZnCl ₂	Poplar wood	Pyroprobe (350, 400, 500, 600)	Packed bed (350, 400, 500, 600)	2.5, 5, 10	-	2000 °C/s for filament	[176] 2011
21	Dolomite and a nickel based catalyst	Pine wood	Sample boat in a heated furnace (700)	Packed bed (600, 700, 800)	-	-	>1000 °C/min	[177] 2004
22	Na/ASA, K/ASA, Cs/ASA, Mg/ASA, Ca/ASA ^a	Pine wood (Canadian)	Packed-bed (450)	Packed-bed (450)	0.5	-	1700 °C/min	[177] 2012
23	Alumina (Specific surface area: 93, 160, 193 and 215), Tetragonal Zirconia, Titania, Zr/Ti	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed-bed (500)	~0.5	<1	-	[147] 2011
24	Fe/Cr	Lignocel HBS 150-500 (beech wood originated)	Packed-bed (500)	Packed-bed (500)	~0.5	-	-	[69] 2000

^a ASA: Alkali-modified amorphous silical alumina.

Table A.4.1. Individual elemental distribution over various pyrolysis products relative to the element (carbon, hydrogen, and oxygen) fed to the system. Values are represented in relative %'s.

	GROUP 1				GROUP 2		GROUP 3		
	Sand	A	A-M1-H	A-M1-L	B	B-M2-A	B-M2-F	G-M2-A	G-M2-F
Carbon balance									
Organics ^a	60.5	51.0	56.9	55.9	63.8	58.5	55.9	58.0	53.4
Water ^b	-	-	-	-	-	-	-	-	-
Char	20.4	17.9	18.1	17.9	18.3	18.8	18.0	15.8	19.5
Coke ^c	-	7.7	1.3	2.8	2.3	2.2	3.6	2.9	4.4
NCG ^d	19.1	23.4	23.7	23.3	15.6	20.6	22.5	23.3	22.7
Hydrogen balance									
Organics ^a	41.0	31.4	28.7	35.9	21.5	35.6	39.3	34.6	34.3
Water ^b	38.5	45.2	50.2	41.6	60.1	44.9	39.8	44.1	42.9
Char	9.8	7.5	7.6	7.5	8.3	7.6	7.1	6.2	8.1
Coke ^c	-	6.8	1.2	2.5	2.0	1.9	3.2	2.6	4.0
NCG ^d	10.7	9.1	12.3	12.4	8.0	10.0	10.6	12.5	10.7
Oxygen balance									
Organics ^a	28.9	8.7	5.4	17.8	2.7	6.1	5.4	5.5	4.4
Water ^b	39.2	46.1	51.1	42.4	61.2	45.7	40.5	44.9	43.7
Char ^e	4.8	4.8	3.6	2.3	5.1	5.9	6.4	5.2	4.4
Coke ^c	-	6.5	1.1	2.4	1.9	1.8	3.0	2.5	3.8
NCG ^d	27.1	33.9	38.7	35.1	29.0	40.5	44.7	41.8	43.7

^a Calculated by difference. ^b Based on the results of Karl Fischer analyses. ^c Coke refers to coke on catalyst. The elemental composition of coke was obtained (the given values were averaged) from Williams and Horne [195]. ^d Derived from micro-GC analyses. ^e Oxygen in char was calculated by difference.

Table A.4.2 Elemental compositions (in wt.%), heating values, and chemical formulae of organics, char, and non-condensable gases with the use of different catalysts.

	<i>GROUP 1</i>				<i>GROUP 2</i>		<i>GROUP 3</i>		
	Sand	A	A–M1–H	A–M1–L	B	B–M2–A	B–M2–F	G–M2–A	G–M2–F
<i>Organics</i> [†]									
C	64.2	80.3	86.5	71.7	92.2	84.8	84.5	85.6	86.1
H	5.5	6.2	5.5	5.8	3.9	6.5	7.5	6.4	6.9
O	30.3	13.5	8.1	22.5	3.9	8.7	8.0	8.0	7.0
HHV [MJ/kg] ^a	24.1	33.6	35.7	28.5	36.1	36.5	37.9	36.8	37.9
Chemical formula	CH _{1.03} O _{0.74}	CH _{0.93} O _{0.13}	CH _{0.76} O _{0.07}	CH _{0.97} O _{0.24}	CH _{0.51} O _{0.03}	CH _{0.92} O _{0.08}	CH _{1.07} O _{0.07}	CH _{0.9} O _{0.07}	CH _{0.96} O _{0.06}
<i>Char</i>									
C	77.4	76.0	79.9	84.7	75.1	73.5	71.5	72.6	78.4
H	4.7	4.0	4.2	4.5	4.3	3.7	3.6	3.6	4.1
O	17.9	20.0	15.8	10.8	20.6	22.8	24.9	23.8	17.6
HHV [MJ/kg] ^b	30.0	28.2	30.6	33.3	28.2	26.6	25.3	25.9	29.6
Chemical formula	CH _{0.73} O _{0.17}	CH _{0.63} O _{0.2}	CH _{0.63} O _{0.15}	CH _{0.64} O _{0.10}	CH _{0.69} O _{0.21}	CH _{0.6} O _{0.23}	CH _{0.6} O _{0.26}	CH _{0.6} O _{0.25}	CH _{0.63} O _{0.17}
<i>NGC's</i>									
C	40.5	40.4	37.4	39.2	34.5	33.3	33.1	35.2	33.9
H	2.8	2.0	2.4	2.6	2.2	2.0	2.0	2.4	2.0
O	56.6	57.6	60.2	58.1	63.2	64.4	64.9	62.4	64.1
LHV [MJ/m ³] ^c	16.1	15.4	14.1	15.4	12.2	11.0	10.7	12.6	11.4
Chemical formula	CH _{0.83} O _{1.05}	CH _{0.59} O _{1.07}	CH _{0.77} O _{1.21}	CH _{0.8} O _{1.11}	CH _{0.77} O _{1.37}	CH _{0.72} O _{1.45}	CH _{0.73} O _{1.47}	CH _{0.82} O _{1.33}	CH _{0.71} O _{1.42}

[†] Dry basis. ^a Calculated based on Milne formula: HHV = 338.2*C + 1442.8*(H-(O/8)) [MJ/kg]. In Milne *et al.* [196]. ^b HHV_{char} = 0.34 × %C + 1.4 × %H - 0.16 × %O, [MJ/kg]. In Ioannidou *et al.* [190]. ^c LHV_{NGC} = (30.0 × CO + 25.7 × H₂ + 85.4 × CH₄ + 151.3 × C_nH_m) × 4.2. In Ioannidou *et al.* [190].

Table A.4.3a Evaluation of catalyst performances in catalytic fast pyrolysis experiments of pine wood performed in lab-scale fast pyrolysis mini-plant, at a reactor temperature of 500 °C. Weight factors of the evaluated criteria were assigned according to targeting on *the deoxygenation requirements*. The best and the worst performances are represented by + + + + and – – – –, respectively.

Criteria	Weight factor	A	A–M1–H	A–M1–L	B	B–M2–A	B–M2–F	G–M2–A	G–M2–F
• Deoxygenation by CO ₂ ^a	8	– – – –	–	– – –	–	++	++++	+	+++
• The yield of organic liquid phase ^{b,d}	7	– – –	– – – –	++++	– –	++	+	+++	–
• H/C ratio of the organic liquid phase ^c	6	+	– – –	+++	– – – –	+	++++	+	+++
• O/C ratio of the organic liquid phase ^c	5	– – –	– – – –	++	++++	– –	++	++	+++
• Coke yield ^b	4	– – – –	++	++++	+	–	– – –	+++	– –
• The production of desirable compounds (<i>i.e.</i> aromatics, phenols, and furans) ^d	3	++++	++	+++	–	– – –	–	– – – –	+
• Energy content in the organic liquid phase (based on HHV) ^c	2	– – –	– –	– – – –	–	+	++++	++	++++
• The percentage of detectable components in the organic liquid phase ^d	1	++++	++	+++	– – –	+	– –	– – – –	–
Score (relative to the best performing catalyst)		47.2	50.9	95.4	65.3	79.6	100	89.4	96.3
Ranking		8	7	3	6	5	1	4	2

^a See Fig. 4.3.; ^b See Fig. 4.2.; ^c See Table A.4.2 in the Supporting Information; ^d See Table 4.2.

Table A.4.3b Evaluation of catalyst performances in catalytic fast pyrolysis experiments of pine wood performed in lab-scale fast pyrolysis mini-plant, at a reactor temperature of 500 °C. Weight factors of the evaluated criteria were assigned according to targeting on *the production of desirable compounds in high yields*. The best and the worst performances are represented by + + + + and – – – –, respectively.

Criteria	Weight factor	A	A–M1–H	A–M1–L	B	B–M2–A	B–M2–F	G–M2–A	G–M2–F
• The production of desirable compounds (<i>i.e.</i> aromatics, phenols, and furans) ^a	8	++++	++	+++	–	---	–	-----	+
• The yield of organic liquid phase ^{a,b}	7	---	-----	++++	--	++	+	+++	–
• Energy content in the organic liquid phase (based on HHV) ^c	6	---	--	-----	–	+	++++	++	++++
• Deoxygenation by CO ₂ ^d	5	-----	–	---	–	++	++++	+	+++
• The percentage of detectable components in the organic liquid phase ^a	4	++++	++	+++	---	+	--	-----	–
• Coke yield ^b	3	-----	++	++++	+	–	---	+++	--
• H/C ratio of the organic liquid phase ^c	2	+	---	+++	-----	+	++++	+	+++
• O/C ratio of the organic liquid phase ^c	1	---	-----	++	++++	--	++	++	+++
Score (relative to the best performing catalyst)		71.0	70.0	100	65.0	81.5	97.5	79.5	98.5
Ranking		6	7	1	8	4	3	5	2

^a See Table 4.2.; ^b See Fig. 4.2.; ^c See Table A.4.2 in the Supporting Information; ^d See Fig. 4.3.

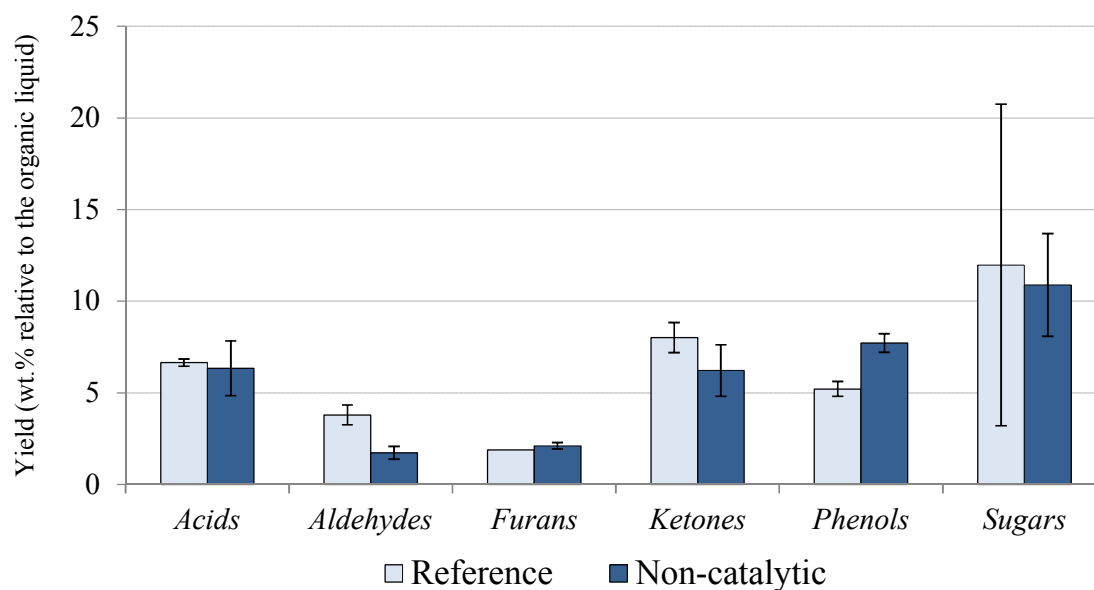


Fig. A.5.1. Comparison of the yields of acids, aldehydes, furans, ketones, phenols and sugars for a reference sample (BTG bio-oil) and the average of five non-catalytic experiments at a T_{reactor} of 500 °C with pine wood as feedstock. Only the most abundant compounds were quantified by GC×GC/MS-FID and their amounts are expressed as wt.% relative to the organic liquid. Error bars represent standard deviations.

Table A.5.1. List of some experimental studies found in the literature dealing with the catalyst regeneration in catalytic pyrolysis of woody biomass.

<i>Ref.</i>	<i>Year</i>	<i>Group</i>	<i>Reactor type</i>	<i>Catalyst type</i>	<i>Number of reaction/regeneration cycles</i>	<i>Type of regeneration procedure</i>
[195]	1995	Williams and Horne	Dual fluidized bed (ex situ)	HZSM-5	5	Outside the bed, single stage regeneration at 550 °C
[125]	2007	Aho <i>et al.</i>	Fluidized bed (in situ)	Acidic H-beta zeolites	1	Outside the bed, two stage regeneration at 250 °C and 450 °C
[104]	2008	Aho <i>et al.</i>	Fluidized bed (in situ)	Beta, Y, ZSM-5 and MOR type acidic zeolites	1	Outside the bed, two stage regeneration at 250 °C and 450 °C
[132]	2010	Aho <i>et al.</i>	Dual fluidized bed (ex situ)	Beta, Y, and ferrierite type acidic zeolites	1	Outside the bed, two stage regeneration at 250 °C and 450 °C
[92]	2011	Carlson <i>et al.</i>	Fluidized bed (in situ)	ZSM-5	10	Within the bed, single stage regeneration at 600 °C
[86]	2013	Paasikallio <i>et al.</i>	Fluidized-bed (in situ)	ZSM-5	2	Within the bed, single stage regeneration at 600 °C

Table A.5.2. Elemental distribution over various pyrolysis products obtained from different catalyst reaction/regeneration cycles (R1 to R8), compared to the reference, non-catalytic (NC) and catalytic fast pyrolysis with fresh catalyst (R0) experiments of pine wood at 500 °C. Results are represented in relative %'s.

<i>Carbon balance, relative % to the carbon in feed:</i>										
	NC	R0	R1	R2	R3	R4	R5	R6	R7	R8
Organics ^a	59.4	51.5	51.0	53.0	54.4	55.2	57.0	60.5	56.8	55.3
Water ^b	-	-	-	-	-	-	-	-	-	-
Char	19.9	19.7	19.7	19.5	19.7	19.7	19.5	19.0	18.4	19.6
Coke ^c	5.1	11.2	10.0	9.6	9.0	9.4	9.3	8.6	7.9	7.5
NCG ^d	15.6	17.6	19.4	17.8	16.9	15.7	14.2	12.0	16.8	17.6
<i>Hydrogen balance, relative % to the hydrogen in feed:</i>										
Organics ^a	45.8	33.2	30.2	29.0	29.1	30.0	28.0	27.5	30.6	36.4
Water ^b	35.2	43.1	46.4	48.9	49.6	48.9	51.9	53.6	49.1	42.7
Char	6.7	6.4	6.5	6.5	6.6	6.8	6.7	6.9	5.9	6.3
Coke ^c	4.5	9.9	8.9	8.6	8.0	8.4	8.3	7.6	7.0	6.7
NCG ^d	7.8	7.4	7.9	7.1	6.7	5.9	5.2	4.4	7.4	8.0
<i>Oxygen balance, relative % to the oxygen in feed:</i>										
Organics ^a	34.2	17.8	13.1	12.0	13.1	14.0	13.3	15.3	15.8	23.5
Water ^b	35.8	43.2	46.6	49.1	49.9	49.1	52.1	53.8	49.3	42.9
Char ^e	1.9	2.9	2.7	3.8	3.3	3.9	3.9	4.1	3.3	1.2
Coke ^c	4.3	9.4	8.4	8.1	7.5	7.9	7.8	7.2	6.6	6.3
NCG ^d	23.8	25.6	28.2	26.0	25.1	24.0	21.8	18.5	23.9	25.1

^a By difference.

^b The relative %'s of hydrogen and oxygen from water were calculated based on the results obtained via Karl Fischer analyses.

^c Coke refers to coke on catalyst. The elemental composition of coke was obtained (the given values were averaged) from Williams and Horne [195]

^d The relative %'s of elements from non-condensable gases were calculated based on the individual gaseous species quantified via micro-GC analyses.

^e Oxygen in char was calculated by difference.

Table A.5.3. Changes of the most prevalent compounds in bio-oil (GC/MS detectable only) resulting from successive reaction/regeneration cycles (R1 to R8) compared with the non-catalytic and catalytic fast pyrolysis with fresh catalyst (R0) experiments, as quantified by GC-MS (wt.% averages on feed basis (a.r.))

	NC	R0	R1	R2	R3	R4	R5	R6	R7	R8
<i>Sugars (3 compounds)</i>	3.79	0.04	0.37	0.58	0.86	1.05	1.26	1.18	1.16	2.09
Levoglucosan	3.22	0.00	0.37	0.58	0.73	0.86	1.26	1.12	1.16	1.84
<i>Aldehydes (2 compounds)</i>	0.67	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Hydroxyacetaldehyde	0.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>Acids (9 compounds)</i>	2.09	0.97	0.86	1.12	1.61	1.57	2.45	2.10	1.58	1.64
Acetic acid	1.50	0.57	0.67	0.78	1.24	1.19	1.99	1.75	1.15	1.16
Propanoic acid	0.29	0.07	0.06	0.09	0.13	0.17	0.21	0.15	0.12	0.13
<i>Furans (12 compounds)</i>	0.57	0.28	0.15	0.11	0.20	0.28	0.18	0.25	0.19	0.12
Furfural	0.22	0.06	0.02	0.03	0.04	0.07	0.08	0.09	0.02	0.02
<i>Ketones (9 compounds)</i>	0.83	0.40	0.41	0.61	0.64	0.66	0.79	0.71	0.64	0.66
2-cyclopenten-1-one	0.16	0.14	0.23	0.30	0.34	0.34	0.40	0.34	0.37	0.34
<i>Phenols (24 compounds)</i>	2.49	2.31	1.94	1.73	2.14	1.62	2.16	1.69	2.45	3.16
1,2-benzenediol	0.51	0.37	0.29	0.25	0.36	0.29	0.38	0.30	0.37	0.50
4-methyl-1,2-benzenediol	0.61	0.43	0.34	0.32	0.40	0.33	0.40	0.33	0.47	0.69
4-ethylcatechol	0.29	0.21	0.16	0.14	0.19	0.14	0.19	0.16	0.21	0.34
2,4-dimethyl-phenol	0.19	0.21	0.17	0.16	0.17	0.14	0.19	0.14	0.21	0.21
4-methyl-phenol	0.11	0.28	0.23	0.20	0.21	0.13	0.20	0.15	0.29	0.27
2-methyl-phenol	0.10	0.17	0.15	0.14	0.16	0.11	0.11	0.12	0.10	0.18
Phenol	0.08	0.28	0.24	0.22	0.23	0.16	0.22	0.17	0.30	0.24
<i>Aromatics (19 compounds)</i>	0.00	0.47	0.52	0.37	0.44	0.26	0.44	0.31	0.43	0.44
Xylene (m, p)	0.00	0.03	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.01
1-methyl naphthalene	0.00	0.24	0.18	0.15	0.13	0.07	0.11	0.08	0.10	0.09
Methyl-1H-Indenes	0.00	0.06	0.09	0.07	0.08	0.04	0.08	0.06	0.08	0.06
Indene	0.00	0.03	0.04	0.03	0.03	0.02	0.03	0.02	0.03	0.02
Indane	0.00	0.01	0.02	0.01	0.01	0.01	0.00	0.01	0.02	0.01
<i>Others (21 compounds)</i>	1.69	0.67	0.47	0.51	0.77	0.90	0.89	0.95	1.11	1.46
1-hydroxy-2-propanone	1.08	0.20	0.09	0.18	0.23	0.40	0.47	0.48	0.57	0.80

Table A.5.4. Distribution of the energy with respect to the pyrolysis products. Values are expressed in relative % to the energy content of pine wood. Calculations were made based on the Dulong equation.

	Bio-oil	Char	Coke	NCG
NC	58.0	19.9	4.6	17.4
R0	49.2	20.0	10.5	20.3
R1	45.3	20.5	9.5	24.7
R2	46.5	21.0	9.7	22.8
R3	47.5	21.4	9.0	22.1
R4	48.8	22.2	9.9	19.1
R5	49.4	22.8	10.2	17.7
R6	52.3	23.4	9.8	14.5
R7	50.2	20.0	8.1	21.7
R8	50.5	21.0	7.3	21.2

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Appendix A

This appendix includes the physical and chemical properties of the catalysts used. This appendix is confidential and can only be accessed by signing a confidentiality agreement.

Appendix B

This appendix includes detailed explanations regarding the findings shown in Chapter 4 in this thesis. This appendix is confidential and can only be accessed by signing a confidentiality agreement.

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Güray

Gent, March 2015

Curriculum Vitae

Güray YILDIZ

Date of Birth: 29 April 1982

Email: guryildiz@gmail.com

Citizenship: Republic of Turkey

Professional experience

- Sept. 2013 – ... Scientific researcher at Ghent University, Ghent, Belgium
2009 – 2013 Doctoral researcher at Ghent University, Ghent, Belgium
2008 – 2009 Scientific researcher at Ege University, Izmir, Turkey
2007 – 2008 Sales representative, Hewlett&Packard Enterprise Services, Izmir, Turkey
2006 – 2007 Tutor of chemistry and mathematics, Izmir, Turkey

Education

- Sept. 2009 – ... Doctor of Philosophy (Ph.D.) in Applied Biological Sciences, Option: Chemistry and Bioprocess Technology.
Faculty of Bioscience Engineering, Department of Biosystems Engineering, Ghent University, Ghent, Belgium.
Promoter: Prof. Dr. ir. Wolter Prins
Co-promoter: Prof. Dr. ir. Frederik Ronsse
Thesis title: *Catalytic Fast Pyrolysis of Biomass*, supported by and collaborated with Albemarle Catalyst Company B.V., Amsterdam, The Netherlands; Biomass Technology Group B.V. (BTG), Enschede, The Netherlands; Sustainable Process Technology Group of University of Twente, Enschede, The Netherlands; Laboratory for Chemical Technology (LCT), Ghent University, Ghent, Belgium.
- 2007 – 2009 Master of Science (M.Sc.) in Chemical Engineering.
Faculty of Engineering, Department of Chemical Engineering (English), Ege University, Izmir, Turkey.
Promoters: Prof. Dr. Levent Ballice, Prof. Dr. Mithat Yüksel
Thesis title: *Hydrogen and/or Methane Production from Glycerol Using Catalytic Gasification Processes with Phosphoric Acid and Salts of Phosphoric Acid in Supercritical Water*. This project was supported by TÜBİTAK (The Scientific and Technological Research Council of Turkey) Engineering Research Group, Project No:107M480.

- 2001 – 2007 Bachelor of Science (B.Sc.) in Chemical Engineering.
Faculty of Engineering, Department of Chemical Engineering (English),
Ege University, Izmir, Turkey.
Supervisor: Prof. Dr. Levent Ballice
Design project title: *Overall Design of a Plant, producing “Cumene from Propylene, Propane and Benzene”*
Graduation thesis title: *Liquefaction of Solid Fuels and Characterization of Liquefaction Products*. Research experiments were (partially) performed in PETKIM Inc.
- 2003 – 2007 Bachelor’s Degree in Business Administration (B.B.A.).
Faculty of Business Administration, Department of Business Administration, Anadolu University, Eskisehir, Turkey.

Scientific publications (by April 2015)

A1 (Articles in international journals with peer review, listed in ISI-Web of Science)

1. **Yildiz, G.**, Ronsse, F., Venderbosch, R., van Duren, R., Kersten, S. R. A., & Prins, W. (2015). Effect of biomass ash in catalytic fast pyrolysis of pine wood. *Applied Catalysis B: Environmental*, 168, 203–211. (IF: 6.007; Q1 in the category of Chemical Engineering)
2. **Yildiz, G.**, Lathouwers, T., Toraman, H. E., van Geem, K. M., Marin, G. B., Ronsse, F., van Duren, R., Kersten, S. R. A., & Prins, W. (2014). Catalytic fast pyrolysis of pine wood: effect of successive catalyst regeneration. *Energy & Fuels*, 28, 4560–4572. (IF: 2.733; Q1 in the category of Chemical Engineering)
3. **Yildiz, G.**, Pronk, M., Djokic, M., van Geem, K. M., Ronsse, F., van Duren, R., & Prins, W. (2013). Validation of a new set-up for continuous catalytic fast pyrolysis of biomass coupled with vapour phase upgrading. *Journal of Analytical and Applied Pyrolysis*, 103, 343–351. (IF: 3.070; Q1 in the categories of Analytical Chemistry, Spectroscopy)
4. Ameloot, N., De Neve, S., Jegajeevagan, K., **Yildiz, G.**, Buchan, D., Funkuin, N.Y., Prins, W., Bouckaert, L., & Sleutel, S. (2013). Short-term CO₂ and N₂O emissions and microbial properties of biochar amended sandy loam soils. *Soil Biology & Biochemistry*, 57, 401–410. (IF: 4.410; Q1 in the category of Soil Science)
5. Djokic, M. R., Dijkmans, T., **Yildiz, G.**, Prins, W., & van Geem, K. M. (2012). Quantitative analysis of crude and stabilized bio-oils by comprehensive two-dimensional gas-chromatography. *Journal of Chromatography A*, 1257, 131–140. (IF: 4.258; Q1 in the categories of Analytical Chemistry, Biochemical Research Methods)

A1 (Articles in international journals with peer review, listed in ISI-Web of Science) submitted and/or in progress

1. **Yildiz, G.**, Ronsse, F., Vercruysse, J., Daels, J., Toraman, H. E., van Geem, K. M., van Duren, R., & Prins, W. (2015). Screening metal doped catalysts in situ for continuous catalytic fast pyrolysis of pine wood. Submitted to *Journal of Analytical and Applied Pyrolysis*. (IF: 3.070; Q1 in the categories of Analytical Chemistry, Spectroscopy)

2. **Yildiz, G.**, Ronsse, F., van Duren, R., & Prins, W. (2015). Challenges in the design and operation of processes for catalytic fast pyrolysis of biomass. Submitted to *Renewable & Sustainable Energy Reviews*. (IF: 5.510; Q1 in the category of Energy & Fuels)

C1 (Articles published in proceedings of scientific conferences and/or symposia)

1. **Yildiz, G.**, Ronsse, F., Prins, W., Assink, D., Gerritsen, L., van Duren, R., & Rosso-Vasič, M. (2011). Catalytic fast pyrolysis of biomass. *European biomass conference and exhibition proceedings* (pp. 1145–1148). Presented at the 19th European Biomass Conference and Exhibition, Berlin, Germany.
2. **Yildiz, G.**, Ronsse, F., Prins, W., Rosso-Vasič, M., Van Duren, R., & Janbroers, S. (2012). Catalytic fast pyrolysis of biomass. *Communications in Agricultural and Applied Biological Sciences* (Vol. 77, pp. 73–77). Presented at the 17th National symposium on Applied Biological Sciences, Katolieke Universiteit Leuven (KUL), Leuven, Belgium.

C3 (Active participation to symposia, conferences, or workshops with oral presentation)

1. **Yildiz, G.**, Ronsse, F., Van Geem, K., van Duren, R., Kersten, S. R., & Prins, W. (2014). Effect of biomass originated ash in catalytic fast pyrolysis of biomass. In A. S. Noskov (Ed.), *CHEMREACTOR-21: XXI international conference on chemical reactors, Proceedings* (pp. 126–127). Presented at the 21st International conference on Chemical Reactors (CHEMREACTOR-21), Delft University of Technology, Delft, The Netherlands.
2. **Yildiz, G.**, Lathouwers, T., Toraman, H. E., Van Geem, K., Ronsse, F., van Duren, R., Kersten, S. R., & Prins, W. (2014). Effect of sequential catalyst regeneration in catalytic fast pyrolysis of biomass. *Analytical and Applied Pyrolysis, 20th International symposium, Conference guide and abstracts* (pp. 129–129). Presented at the 20th International symposium on Analytical and Applied Pyrolysis (PYRO 2014), Birmingham, United Kingdom.
3. **Yildiz, G.**, Au-Yeung, K.-M., Ronsse, F., van Duren, R., & Prins, W. (2012). Catalytic Fast Pyrolysis of Biomass. *XX International conference on chemical reactors "CHEMREACTOR-20": abstracts* (pp. 103–104). Presented at the 20th International conference on Chemical Reactors (ChemReactor 20), Luxemburg.
4. **Yildiz, G.**, Ronsse, F., Au-Yeung, K.-M., Rosso-Vasic, M., Van Duren, R., & Prins, W. (2012). Catalytic fast pyrolysis of biomass. *Analytical and Applied Pyrolysis, 19th International symposium, Abstracts* (pp. 95–95). Presented at the 19th International symposium on Analytical and Applied Pyrolysis (Pyrolysis 2012), Johannes Kepler University, Linz, Austria.
5. **Yildiz, G.**, Ronsse, F., van Duren, R. & Prins, W. (2015). Catalytic fast pyrolysis of biomass: From lab-scale research to industrial applications. *European biomass conference and exhibition proceedings*. Presented at the 23rd European Biomass Conference and Exhibition, Wien, Austria.

C3 (Active participation to symposia, conferences, or workshops with poster presentation)

1. **Yildiz, G.**, Ronsse, F., & Prins, W. (2014). Testing the stability of a ZSM-5 catalyst under biomass fast pyrolysis conditions. *Applied Biological Sciences, 19th National symposium, Abstracts*. Presented at the 19th National symposium on Applied Biological Sciences, Gembloux, Belgium.

C3 (Contributions to oral presentations or posters)

1. Van Geem, K., Toraman, H. E., Schietse, M., Borén, E., Vanholme, R., Gerber, L., Djokic, M., **Yildiz, G.**, Ronsse, F., Prins, F., Sundberg, B., Boerjan, W., & Marin, G.B. (2013). Biomass reaction engineering driving genetic modification. *American Institute of Chemical Engineers Annual meeting, Abstracts*. Presented at the 2013 American Institute of Chemical Engineers Annual meeting (AIChE), San Francisco, CA, USA.

Invited reviewer in international scientific journals

Energy Conversion and Management (Elsevier), Biomass & Bioenergy (Elsevier), Chemie Ingenieur Technik (Wiley-VCH).