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In: 19th European biomass conference and exhibition proceedings (2011), 1145-1148.

To refer to or to cite this work, please use the citation to the published version:

Yildiz, G.; Ronsse, F.; Prins, W.; Assink, D.; Gerritsen, L.; van Duren, R. & Rosso-Vasic, M. (2011). Catalytic fast pyrolysis of biomass. Proceedings of the 19th European Biomass Conference and Exhibition, June 10 - 14, 2011, Berlin, Germany, 1145 - 1148. Doi: 10.5071/19thEUBCE2011-OB8.1

CATALYTIC FAST PYROLYSIS OF BIOMASS

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ABSTRACT: Fast pyrolysis is one of the techniques considered for the production of so called “second generation” biofuels and green chemicals. The produced “bio-oil” is just an intermediate which needs subsequent treatment like fractionation and/or isolation in combination with catalytic upgrading to the desired final products. The objective of this research is to investigate possible beneficial effects on the bio-oil quality of various catalysts applied inside the pyrolysis reactor in relationship with the applied process conditions. First experiments have been carried out in a fully controlled continuous mini-plant designed and constructed by BTG Biomass Technology Group BV on basis of auger reactor technology for (catalytic) biomass fast pyrolysis. The catalyst samples were provided by Albemarle Catalyst Company BV. The experimental reproducibility has been checked by repetition of several non-catalytic experiments under identical conditions. Of these tests the average yields on as received basis are 67.3, 14.7, and 18 wt % for bio-oil, gas, and char, respectively. Experiments were performed at a fixed pyrolysis temperature of 500 °C and pine wood was selected as feedstock. Two different catalysts were also tested with an acceptable mass balance closure. Some physical properties, such as; water content, pH and TAN of liquid product and degree of devolatilization of feed were analyzed. Elemental analyses of virgin bio-oil and water phases of catalytic bio-oils were carried out. Catalyst impact on the yield distribution and product properties was observed. In this paper some preliminary results are presented.

Keywords: biomass, fast pyrolysis, catalysis, biofuel, biomass to liquid (BtL), pilot plant

1 INTRODUCTION

Exploitation of clean renewable energies has attracted great attention due to the declining fossil fuel reserves and the ever-increasing greenhouse effects produced through fossil fuel utilization. These possible future shortages and environmental concerns have boosted research into alternatives for fossil-derived products. As an alternative energy source, biomass is abundantly available worldwide and this considered to be renewable and clean. Utilization of biomass as chemical feedstock faces problems due to its complex structure and the difficulty to separate its components in an economically feasible way. However, biomass is the only renewable energy source available that can deliver a solid, liquid and gaseous fuel. Two main types of processes can be used to convert biomass to bioenergy: thermo-chemical and bio-chemical/biological processes. Generally, thermo-chemical processes have higher efficiencies than bio-chemical/biological processes in terms of the lower reaction time required and the superior ability to destroy most of the organic compounds [1]. The type and quantity of biomass feedstock; the desired form of the energy, i.e. end-use requirements; environmental standards; economic conditions; and project specific factors are some factors that influence the suitable conversion process [2]. As an emerging advanced technology, fast pyrolysis is an integrated process for production of a liquid fuel that can be used directly and as an intermediate pre-treatment step to convert solid biomass into a higher energy content transportable liquid for subsequent processing for heat, power, biofuels, and chemicals [3].

Fast pyrolysis is meant to convert biomass into a maximum quantity of liquids, and currently of particular interest as the liquid product can be stored and transported, and used for energy, chemicals or as an alternative energy carrier. Fast pyrolysis processes are

characterized by a high rate of particle heating to moderate temperatures around 500°C, and the rapid cooling of the produced vapors to condense the liquids. This yields a maximum quantity of dark-brown mobile liquid (bio-oil) with a heating value roughly equal to that of wood, which is approximately half the heating value of fossil fuel oil [4]. A critical review on bio-oil is documented elsewhere [5].

Bio-oil is a mixture of hundreds of different, highly oxygenated chemical compounds. It is unsuitable for application as a transportation fuel due to its adverse properties (e.g. instability, acidity) 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.). In order to improve the quality of crude bio-oil in relation to biofuel applications, and to reduce the upgrading costs, pyrolysis of biomass can be performed in the presence of suitable catalysts.

Catalytic fast pyrolysis, either by adding catalyst particles to the reactor (in-situ) or by secondary fixed-bed conversion, is meant for removal of the oxygen and catalytic cracking of the high molecular weight compounds in the pyrolysis vapours. Details of the desired function(s) of the catalyst and the product application specifications are largely unknown. Recent papers report on experiments with micro-pyrolysis plus GC-MS, zeolite cracking in small laboratory units, or treatment of pyrolysis vapours in small fixed bed reactors. While screening a wide variety of catalysts, the production of useful hydrocarbons is observed indeed, mostly aromatics, but the yield is low due to excessive formation of coke and permanent gases. This research is focused on testing catalyst pre-screened by Albemarle, in a dedicated mini-plant that allows variation of the catalyst loading and contact times while producing larger samples in continuous operation. The intention of the

catalyst testing is to suppress coke and gas formation and to increase the yield of a hydrocarbon fraction that can be used for co-feeding refinery units in the production of transportation fuels. Reports from NREL show that fast pyrolysis oil upgraded by hydro-de-oxygenation (HDO) can be produced at a very competitive price compared to other biomass conversion technologies. Catalytic pyrolysis could reduce or, ideally, even avoid the need for HDO upgrading.

2 MATERIALS AND METHODS

2.1 Feedstock

Pine wood with a moisture content of 5 wt% (as-received basis) and a number-average particle size of 1 mm (maximum size = 2 mm) was the reference feedstock and supplied by BTG. The ash content (dry-basis) of biomass was 0.45 wt%. An excess of pre-heated silica sand with a mean diameter of 250 μm and a particle density of 2600 kg/m^3 (bulk density = 1600 kg/m^3) was used to drive the biomass devolatilization. Two types of catalysts, namely; catalyst A and catalyst B were pre-screened and supplied by Albemarle Catalyst Company BV. To prevent water accumulation in the final liquid product, these catalysts were calcined for moisture removal.

2.2 Mini-plant

Catalytic fast pyrolysis experiments have been carried out in a fully controlled continuous mini-plant designed and constructed by BTG based on auger reactor technology (Fig.1). Table I shows the design specifications of the test unit. The mini-plant enables the production of larger bio-oil samples (typically 0.5 litre/run) suitable for a full characterization, even in the case of multiple phases. The changes in temperatures, pressures and flow rates were observed and controlled online. A reactor temperature of 500°C has been applied in these first experiments. For both non-catalytic (sand) and catalytic experiments, biomass and heat carrier flow rates were selected as 200 gr/h and 6 kg/h, respectively and were precisely controlled. The whole system was continuously purged with a controlled flow rate of nitrogen gas to maintain an inert condition. For catalytic runs, a catalyst/sand ratio of 1:3 were selected (Tables II and III).

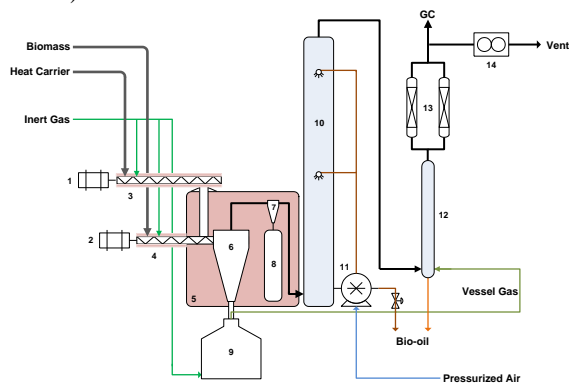


Figure 1: Flow diagram of the mini-plant: (1) heat carrier screw rotor; (2) biomass feed screw rotor; (3) heat carrier screw; (4) biomass feeding/auger screw; (5) furnace; (6) pyrolysis reactor vessel; (7) cyclone; (8) cyclone vessel; (9) sand and char collection vessel; (10) spray condenser; (11) liquid circulation pump; (12)

secondary condenser; (13) cotton filters; and (14) gas flow meter

Table I: Design specifications of mini-plant

Technology	Catalytic Fast Pyrolysis
Max. temperature	600 °C
Max. biomass feed flow rate	500 gr/h
Max. catalyst / heat carrier flow rate	10 kg/h
Max. inert gas flow rate	150 l/h
Pressure	Atmospheric
Vapour residence time	max. 1 s
Biomass residence time	max. 1 s

Table II: General process conditions for sand runs

Fast pyrolysis temperature	500 °C
Biomass flow rate	200 gr/h
Sand flow rate	6 kg/h
Sand / Biomass ratio	30:1
Nitrogen flow rate	110 l/h

Table III: General process conditions for catalytic runs

Fast pyrolysis temperature	500 °C
Biomass flow rate	200 gr/h
Blend flow rate	6 kg/h
Catalyst / Sand ratio	1:3
Catalyst / Biomass ratio	7.5:1
Nitrogen flow rate	110 l/h

2.3 Experimental

For each run, fresh biomass and sand (catalyst blend for catalytic runs) were loaded in the hoppers. After making all connections within the system, the leakages were checked by observing the pressure increase. Later, the heating-up process started under inert gas flow through the system. Once the system reached its specified temperature set point, all elements were switched on including feed and sand conveyors and condenser pump. Experiments were started after 30 minutes in order to minimize the temperature and inert gas flow rate gradients. After that, the biomass and heat carrier inside the separate hoppers were conveyed through the reactor using screw feeders. They contacted within the last section of the biomass feed screw and the pyrolysis reaction took place at this point at a maximum residence time of one second. During the reaction, pyrolysis vapours were produced and passed through the cyclone and reached the condenser. The mini-plant has a vapor condensing system that consists of a jacketed spray condenser combined with a peripheral pump. Before each experiment, a known amount of paraffinic solvent was fed to the condenser as spraying and startup liquid. The reason for selecting this liquid was that it has a low solubility in pyrolysis oil and therefore facilitated nearly full decantation of the oil produced. Any bio-oil components dissolved in the paraffinic solvent can be quantified as well. Further advantage of this compound is the easy peak identification in GC-MS and 2D-GC analyses. After each run, the produced liquid together with the startup liquid was tapped from the condenser. However, there was still a considerable amount of viscous liquid in the condenser which was stuck to the condenser walls. In the catalytic runs, this portion was mostly the heavy fraction of the produced oil. To get this oil out, the condenser was flushed several times with acetone until there was no liquid product left in the system. This was determined by observing the color change in tapped acetone. This mixture was composed of acetone, bio-oil (or heavy fraction) and some paraffinic

solvent. Excess acetone was removed in a rotary evaporator and the remaining liquid was included in the mass balance. However, there could be some disadvantages with this technique such as the loss of some acetone soluble compounds with the removed acetone and possible composition change in catalytic heavy fractions. Also, the mass of condensed aerosols in the cotton filters was added to total liquid amount.

While pyrolysis vapours moved through the condenser, produced char and sand (spent catalyst) particles fell down to the solid collection vessel that lies below the reactor furnace. After each experiment, the heat carrier and char mixture that was collected in the collection vessel was sieved first by hand and then by using a mechanical sieve shaker. However, this well sieved char was still contained a significant portion of the sand that was stuck onto its surface. Because of the weighing difficulties of this product, the char yield was calculated from the overall mass balance.

The volume of gas was determined by observing the gas meter readout. The gas meter is located just before the vent and quantifies the gas flow through the system. The gas sample was taken by using a gas-tight syringe and analyzed in a micro-GC. The gases that were identified by micro-GC are: H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈.

2.3 Product analysis

The produced bio-oil samples were characterized by measuring their water content, pH value, total acid number, and total organic carbon along with an ultimate analysis. Also to determine the chemical composition of the oil, GC-MS and 2D-GC analysis were carried out. However, there is still a room for the improvement of GC-MS analysis. In each run, gas samples were taken by a gas-tight syringe and analyzed by a micro-GC. In total 8 samples were injected and the averages were used for gas yield calculations. The details about the used analytical equipment and the GC-MS results will be given in the following publication.

3 RESULTS AND DISCUSSIONS

3.1 Product yields

Significant numbers of non-catalytic experiments were carried out to reach the desired product yields and the results were compared with BTG's own fast pyrolysis pilot plant (Fig.2). The results were comparable.

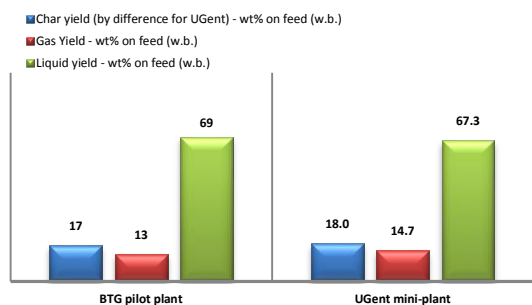


Figure 2: Product yields - BTG pilot plant vs. mini-plant.

Figure 3 shows the product yields of (non-catalytic), catalyst A and catalyst B runs. Decreases in liquid yields while the increases in char and gas yields can be observed. The liquid distributions are shown in Figure 4.

Compared with the non-catalytic bio-oil, the organic phase amounts decrease while water phase amounts increase. This showed that the use of catalysts enhances the removal of water from the oil fraction.

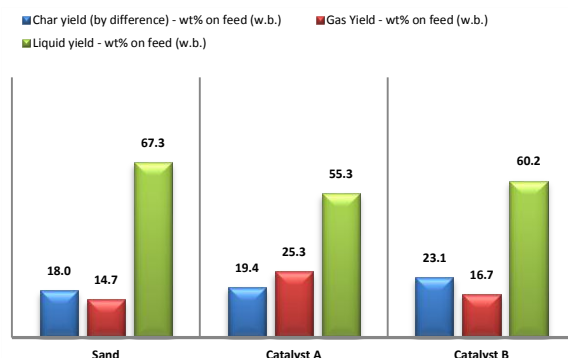


Figure 3: Product yields: sand, Catalyst A and Catalyst B.

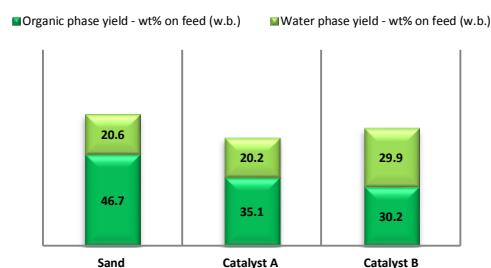


Figure 4: Organic and non-organic fractions of product bio-oils.

3.2 Acidity of produced liquids

The cause of acidity in bio-oils is the organic acids from biopolymer degradation [5]. In Figure 5, the total acid number (TAN) and the pH value changes with the use of Catalyst A can be observed. Catalyst application has a crucial impact on bio-oil acidity.

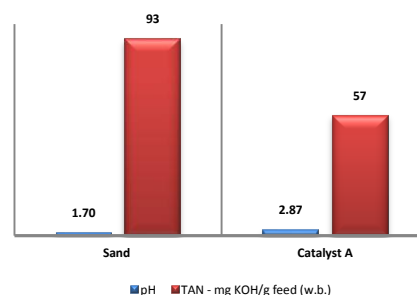


Figure 5: Acidity of liquid products. Sand vs. Catalyst A.

3.3 Non-condensable gas composition

Volumetric gas compositions of the non-condensable gases are shown in Figure 6. CO_x represents the summation of CO and CO₂ gas volumetric percentages. The increase in CO_x value indicates the removal of oxygen from bio-oil in the forms of CO and CO₂. With the catalyst application, the increase was observed.

3.4 Elemental analysis

In Figure 7, elemental analysis of the biomass, non-catalytic bio-oil, water phases of catalyst A and B are shown. The elemental compositions of biomass and bio-oil were similar. The increase in oxygen levels in water

phases represents the presence of water in this liquids.

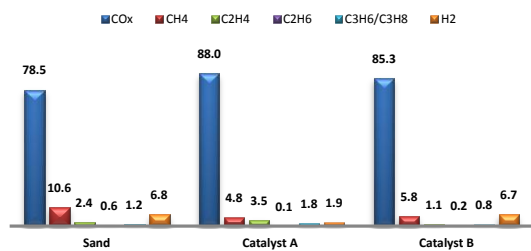


Figure 6: Non-condensable gas compositions (vol%)

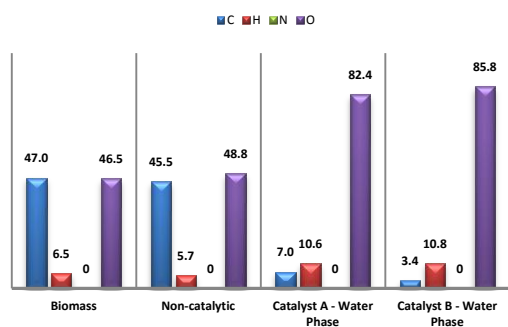


Figure 7: Elemental analysis results of biomass, non-catalytic bio-oil, water phases of catalyst A and B.

3.5 Oxygen removal

Oxygen removal is the most important parameter to observe the impact of a catalyst in the fast pyrolysis process. The oxygen is released from bio-oil in the forms of CO, CO₂ and water. Figure 8 shows the comparison of oxygen removal with the use of catalysts A and B.

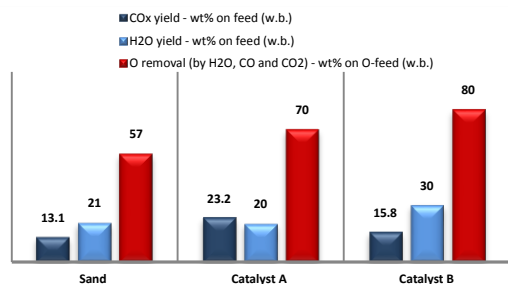


Figure 8: Oxygen removal from bio-oil in the form of COx and water.

4 CONCLUSIONS

The mini-plant that was constructed by BTG was used for non-catalytic and catalytic experiments. Two types of catalyst materials pre-screened and supplied by Albemarle Catalyst Company BV, namely; catalyst A and B were tested in-situ. With the use of catalysts, the liquid yields decreased while gas and char yields increased. The increase in water and CO_x yields in catalytic bio-oils can be concluded as the removal of oxygen from bio-oil in the form of water, CO and CO₂ was achieved. Decreased acidity confirmed the impact of catalysts on the bio-oil quality.

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6 ACKNOWLEDGEMENTS

The authors would like to express sincere thanks to Prof. H.J. Heeres (University of Groningen) and his coworkers for the elemental and preliminary GC-MS / 2D-GC analyses.