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THERMO-CATALYTIC PROCESSES FOR BIOFUEL PRODUCTION

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CICLO XXIX

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DEVELOPMRNT OF CONTINUOUS REACTION SYSTEM FOR HYDROTHERMAL GASIFICATION OF BIOMASS AND MODEL COMPOUND

Abstract

Nowadays, research on biofuel have attracted a tremendous attention as a consequence of the need for the world to face the challenges of global warming, environmental pollution and depletion of fossil fuel reserves. In the case of diesel, the bio-product has different advantages with respect to petroleum derived one, such as sustainability, biodegradability, non-toxicity, lower harmful emissions, higher flash point, excellent lubricity and superior cetane number.

Triglycerides (lipids) are considered the most important renewable resource to obtain liquid biofuels. They can be obtained from plants, animal fat and aquatic organisms. Recently, microalgae have been indicated as a potential source of triglycerides able to meet large energy demands of the fuel market.

Various methods to obtain biofuel have been proposed and studied. The main route of transformation of triglycerides into energy carriers is the transesterification with alcohol (usually methanol and ethanol) to obtain fatty acid methyl or ethyl esters (FAME or FAEE) as biodiesel, and glycerol as co-product.

The interesterification of oils and fats with methyl acetate provides a promising alternative to transesterification because this synthetic route leads to formation of methyl esters (FAME) and triacetin as co-product, instead of glycerol. FAME and triacetin which are perfectly miscible each other and can be used as a whole as biodiesel thus avoiding any need of separation.

Transesterification and interesterification can take a place in supercritical conditions for the alkyl-donor without catalyst, but in this case elevated temperatures and high pressures are needed. Both processes require active catalyst at moderate temperatures. The homogeneous catalysts (both acid and base) are usually adopted for these processes, but their use causes environmental problems and increases the cost.

Heterogeneous catalysis could improve the performance of the transesterification and interesterification processes while allowing easy catalyst separation and recovery from the products mixture.

Another method for the conversion of triglycerides to biofuels is their hydrogenation and/or deoxygenation. This treatment leads to the formation of long straight chain hydrocarbons. The

industrial application of this technology depends on the development of the catalytic system. Recently, many researchers have tested heterogeneous catalysts for the deoxygenation of oils or fatty acids, but the goal of identifying a catalytic system able to make the process economically feasible is still not been reached. Some strategies have been developed to improve the economy and the sustainability of this process, like, for example, the use of glycerol produced by the transesterification or the hydrolysis of triglycerides. On this regard, the possibility to convert glycerol into hydrogen needed for the hydrotreatment of fatty acids into alkanes is one of the most promising scenarios.

Supercritical water gasification (SCWG) is an interesting technology for the exploitation of organic compounds and wet biomass. This technology allows to transform organic compounds and wet biomass using water at a temperature and pressure above its critical point ($T > 374.15$ °C; $P > 22.1$ MPa) to obtain a high amount of hydrogen as well as light hydrocarbons and CO_x.

After an overview of the world energy situation and the potential of microalgae as source of triglycerides, in this thesis the attention was focused on transesterification and interesterification processes using tin-based heterogeneous catalysts.

The attention was then shifted on the hydrothermal processes of deoxygenation of fatty acids and of glycerol gasification in presence of Raney nickel catalyst.

The last chapter is dedicated to the description of a continuous lab-scale plant for the treatment of organic compounds in supercritical water and to the presentation of some preliminary testing of non-catalytic gasification.

Chapter 1

BIOFUEL FROM MICROALGAE

1.1 World energy situation

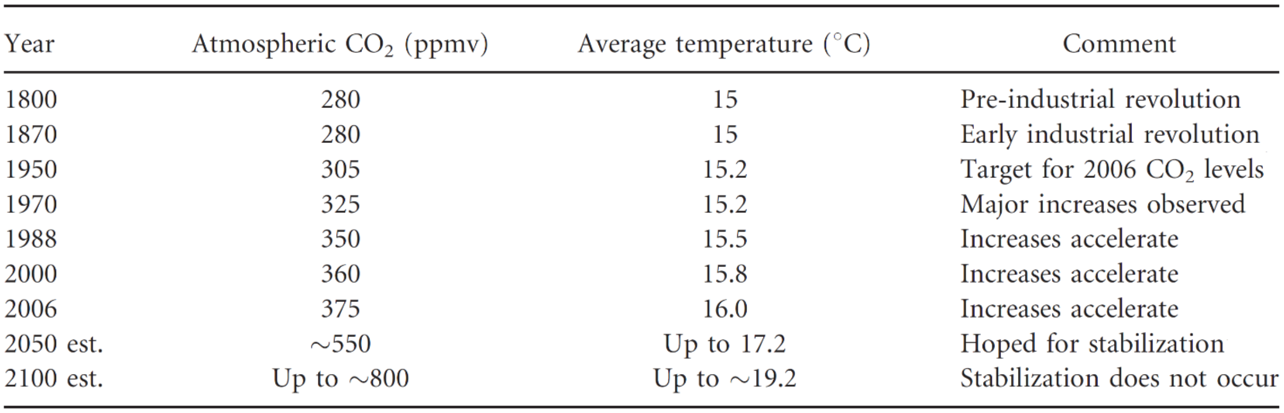
The growing need for energy will lead to a global energy crisis due to the limited availability of fossil resources. Moreover in recent years climate change is occurring that are mainly due to high CO_2 gas emissions from combustion of fossil fuels and that have been an additional reason to search for new energy sources. Among the greatest challenges facing society in fact, is the development of technologies able to obtain renewable green energy at an acceptable cost [1,2]

To be viable the transition from dependence on fossil fuels to renewable energy requires a high investment that involves both the technology, both the infrastructure and the company. It also required some integration between different types of renewable energy since all forms albeit realistically feasible, have strengths and weaknesses features. For example solar and wind power are intermittent sources of production over time and therefore it is desirable that a different technology allows to store some of this energy into chemical such as hydrogen and other fuels, easy to earn and spend [2].

1.2 Biomass role

It is estimated that anthropogenic activities around the world consume about 13 TW of energy 80% of which come from the burning of fossil fuels (oil 43%, natural gas 40%, coal 17%) [3,4,5]. The dependence on non-renewable sources exposes humanity to three major risks. The first related to the depletion of the deposits which would lead to an energy crisis, the second risk stems from geopolitical consequences due to the heterogeneous distribution of the deposits, which have important effects on the economy and on society. The third risk, now considered the most important to address because it is the most immediate, is climate change. The sudden increase of carbon dioxide (CO_2) in the atmosphere, due to human activities have already caused weather variations that can be dramatically lasting and profound [3].

According to estimates by the exploitation of non-renewable fuel we put 6 Gton every year carbon as CO_2 [6]. In a few years the concentration of CO_2 has increased from 280 ppm to 400 ppm, an increase since the first industrial revolution and become faster and faster. Figure 1.1 shows values of CO_2 into the atmosphere and the average global temperature of two centuries. The temperature, as a result, recorded a significant increase caused by the greenhouse effect. Some authors argue that the continuing growth in energy demand would lead to about 550 ppm by 2050 the level of CO_2 in the atmosphere if fossil deposits were still exploited [3]. If the concentration you cannot stabilize within 550 ppm temperature increase could lead to irreversible climate change with extreme weather events such as hurricanes melting of glaciers and elevations of the ocean water level [6]. The impact of the events are not evenly distributed throughout the Earth, therefore, there are far more areas at risk where the floods or droughts are already making record the first alarm [6,7].



Year	Atmospheric CO_2 (ppmv)	Average temperature (°C)	Comment
1800	280	15	Pre-industrial revolution
1870	280	15	Early industrial revolution
1950	305	15.2	Target for 2006 CO_2 levels
1970	325	15.2	Major increases observed
1988	350	15.5	Increases accelerate
2000	360	15.8	Increases accelerate
2006	375	16.0	Increases accelerate
2050 est.	~550	Up to 17.2	Hoped for stabilization
2100 est.	Up to ~800	Up to ~19.2	Stabilization does not occur

Figure 1.1. CO_2 concentration in the air since 1800 and average temperatures. The figure also shows the future estimates and brief comments.

To reduce the potential climate risk is necessary to reduce or eliminate dependence on fossil energy sources and use so-called carbon neutral, or use those energy sources whose net CO_2 balance between the fixation from the atmosphere during fuel production and the emissions due to the use of the fuel is zero [3]. Renewable energies as such would remove even the first two mentioned risks, since they are inexhaustible sources and energy dependence of the individual source is potentially minimized.

Fossil fuels have been used until today because they are the ideal energy sources: they have a high energy density convertible in different forms (heat, electricity, motive force) as needed. Renewable energy to replace the current energy system will need to meet the same demands and this will only be possible when we can produce renewable energy on a large scale with competitive costs [3].

Among the various options for the production of renewable energy with carbon neutral, biomass represents an interesting technology with a high production potential and that presents many options.

1.3 Options and Principles of Biomass Energy

Biomass is the organic fraction produced by living organisms like animals, plants and microorganisms. Biomass can have different composition depending on its origin, such as food, cellulosic material, food and industrial waste or microorganisms, and according to the type of energy source that can be drawn, ethanol, butanol, methane and hydrogen, electricity or biodiesel [3].

Each option of use of biomass has advantages and disadvantages. However, each option has as its primary source of energy sunlight: the different options have in common the ability to capture solar energy. The biomass energy is considered renewable because its source is the sun, and is considered C-neutral because the energy storage time through photosynthesis is comparable to the time of use for human activities, unlike fossil fuels for which energy storage requires millions of years.

To understand if the biomass alone is able to meet the world energy needs, one must ask whether it has the ability to capture 10 TW of solar energy. The total incident solar energy on the earth's surface amounts to 173000 TW [4], which is 17000 times that used by humans. All photosynthetic organisms on the Earth's surface can capture approximately 140 TW per day [8] of solar energy that is about 10 times the energy demand of the society. It must be considered that a large part of the photosynthetic activity must grant the natural balance of the planet because it is the basis of the food chain of all living beings including humans. This means that 10% of photosynthetic resources cannot be converted into energy, without destroying the balance of the ecosystem.

This suggests that the biomass energy should be strengthened to increase its capacity to capture energy, so one has to choose from the options with the highest production potential.

1.4 Biomass options cannot achieve sufficiently large scale

In general, biofuels obtained from processing of biomass were classified into first, second and third generation depending on the source of biomass from which they are derived. The first-generation biofuels are those obtained from biomass of food use, such as ethanol obtained from sugar cane. These fuels although widely used, will fail to meet sustainability criteria for the production of energy because they utilization adversely impact food availability. Growing plants for the large-scale production of fuel would require a high agricultural area to be allocated to these crops with consequent rise in prices of food for humanity [7,9]. In addition, the net bioenergy obtained from the cultivation, harvesting and processing of corn to make ethanol is only about 10% of that obtained, while 90% is used to meet the energy costs of individual processes [10]. Another approach to biofuel produced from agricultural areas is the use of oil produced from oil plants such as soybean, sunflower and rapeseed. From the oil extracted from these plants, one can obtain biodiesel which is a high-quality transportation fuel. The net energy yield is higher than the bioethanol from corn, since the aliphatic long chain that make biodiesel are naturally immiscible in water, and the separation costs are minimized [3].

Currently only 1% of the agricultural areas are dedicated to the production of biodiesel and ethanol and only 1% of the fuel needed at the global level is satisfied with this production [11].

Finally, the massive use of first-generation fuels could have a negative impact on the ecosystem, as they require a high use of fertilizers, pesticides and fresh water. As a result the pollution of water and soil erosion [12], are among the most obvious effects.

Second generation biofuels, i.e. those from the agricultural and food industry waste, could enhance the production of energy and make less dangerous the environmental impact. To this category belong biomass pruning waste from agricultural and forestry areas, straws of cereals and residues from wood processing. These fractions mainly consist of cellulose, hemicellulose and lignin. Some plants with particular characteristics can be selected to be grown on marginal lands, without the use of water or fertilizers [11]. The conversion of this biomass into energy sources, would meet approximately 7% of the total annual consumption of the United States energy [13]. Waste also often cause serious environmental damage, and their collection and conversion into energy would provide a huge benefit to environmental quality.

Being the residue from living organisms, the starting material is usually chemically very complex, normally contain a mixture of carbohydrates, proteins, lipids and nucleic acids. The use of this biomass requires pretreatment chemical, physical and enzymatic before converting carbohydrates into ethanol [3]. The technology, still are not mature for large-scale development of this biomass and costs are still prohibitive.

The third-generation fuels are that category of fuel derived from aquatic microorganisms. These organisms are apt at producing biomass without competing with agricultural products and without causing environmental problems [14]. This option may be valid for the production of biomass in a large scale since it has the potential to be technically and economically feasible [11].

Conditions for a technically and economically feasible source of biofuels are [11]: it should be competitive or cost less than petroleum-based fuels, should require minimal use of soil and water, and should lead to improved air quality. The judicious exploitation of microalgae could meet these conditions and therefore make a significant contribution to meeting the demand for primary energy, while providing environmental benefits [15].

1.5 Potential role of biofuels from microalgae

The advantages of using biofuels derived from microalgae indicated in literature are [11]: (a) microalgae are capable of producing all the year, therefore, the productivity of microalgae oil crops exceeds the yield of the best oil crops; (b) grow in aqueous media, but they need less water than land crops; (c) microalgae can be grown in brackish water on non-arable land, minimizing the environmental impacts associated with the exploitation of the soil, (d) microalgae have rapid growth potential and many species have high content of oil; (e) can improve air quality, since microalgae can make bio-fixation of CO_2 (1 kg dry algal biomass use approximately 1.83 kg of CO_2); (f) nutrients for growing microalgae can be obtained from waste water, therefore, they are potentially usable for the treatment of organic effluents from the food industry; (g) the cultivation of algae does not need herbicides or pesticides application; (h) can also co-produce valuable products such as proteins and residual biomass after the extraction; (i) the biochemical composition of the algal biomass can be modulated by varying growth conditions, therefore, the oil yield can be significantly improved; (l) microalgae are capable of producing bio-hydrogen.

Despite its inherent potential as a biofuel resource, many challenges have prevented the development of biofuel technology from microalgae. Sustainability is the key to the management of natural resources and socio-economic activities, all of which are interdependent. For the sustainable development of microalgae, technologies and research must help to improve several key factors of production. First, the selection of species must balance the requirements for the production of biofuels and the extraction of high-value co-products [16] also have to improve photosynthetic efficiency, reducing evaporation losses and improve the diffusion of CO_2 in aqueous media [11]. The technologies must be developed to improve the net energy balance and the scale-up problems.

1.6 Biology of microalgae

Algae are one of the oldest forms of life. Microalgae are unicellular and multi-cellular organisms, including both prokaryote and eukaryote microalgae. The most important classes are: green algae (Chlorophyta), red algae (Rhodophyta) and diatoms (Bacillariophyta).

Algae can be autotrophic or heterotrophic. The first require only inorganic compounds such as CO_2, salts and a source of light for growth, while the latter are non-photosynthetic therefore require an external source of organic compounds and nutrients as an energy source. Some photosynthetic algae are mixotrophic, i.e. they have the ability to run both photosynthesis or acquiring exogenous organic nutrients [11].

For autotrophic algae, photosynthesis is a key component of their survival. They convert sunlight and CO_2 absorbed by chloroplasts in adenosine triphosphate (ATP) and O_2, the energy currency used at the cellular level, which is then used in respiration to produce energy to support growth [11]. Only the photosynthetically active radiation of wavelengths between 400 and 700 nm, representing 42.3% of the total energy from the spectrum of light is captured. The captured energy is used in the Calvin cycle to produce carbohydrates using molecules of CO_2 and H_2O in the summary process from the reaction equation:

$$6CO_2 + 6H_2O + \text{photons} = C_6H_{12}O_6 + 6O_2$$

It has been estimated that theoretically only a maximum fraction of 13% of the energy absorbed by the cell is converted into chemical energy. In reality, the majority of terrestrial plants are able to convert about 2% of the radiation, while for the microalgae one can reach 7% [11].

1.7 Technologies for the production of microalgae biomass

Under natural growth conditions, photosynthetic organisms absorb sunlight, carbon dioxide from the air and nutrients from the aquatic medium. Therefore, the artificial production must groped to replicate and improve the optimum natural growth conditions.

For production systems of outdoor algae, the light is usually the limiting factor [17]. To address the limitations in natural growth conditions with sunlight, artificial means employ lamps for the cultivation of algae on pilot plants, but the energy input is very expensive.

The inorganic nutrients necessary for the production of algae include nitrogen, phosphorus and silicon [18]. Silicon is only important to certain groups such as diatoms. Some species of algae can fix nitrogen from the air in the form of NO_x [19], but most of microalgae require it in a soluble form such as urea [20]. Phosphorus is of minor importance and it is required in very small quantities during the growth cycle algal, but must be supplied in excess of basic requirement because phosphate ions bond with metal ions, as a result, not all of the added phosphorus is bioavailable [21].

Currently, the photoautotrophic production is the only method that is technically and economically feasible for large-scale production of algae for the production of biomass. Two systems that were employed are based on open pond and closed photobioreactors technologies. Between open systems the raceway ponds are the most widely used artificial system. They are typically constituted by a closed circuit, oval recirculating channels (see Figure 1.2). Mixing and circulation are needed to encourage the growth of algae and productivity [11].

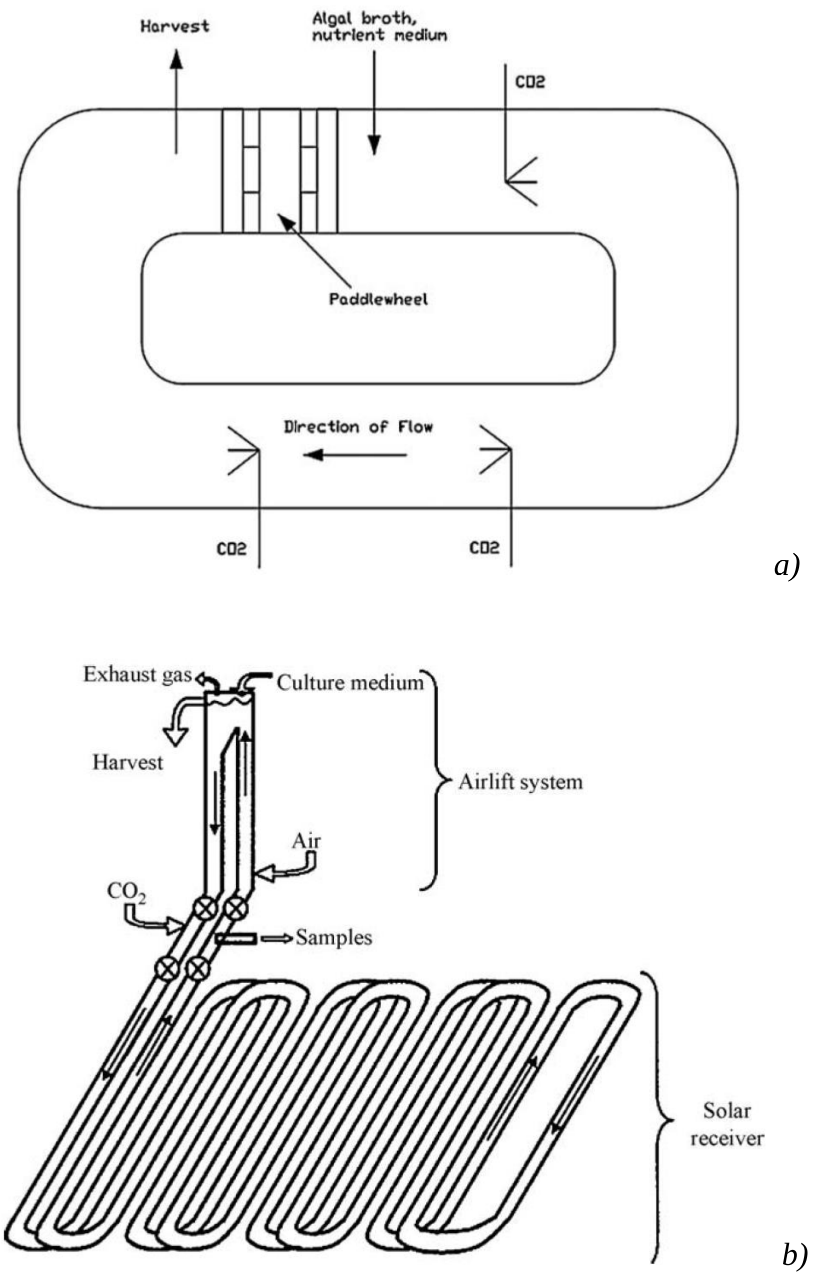


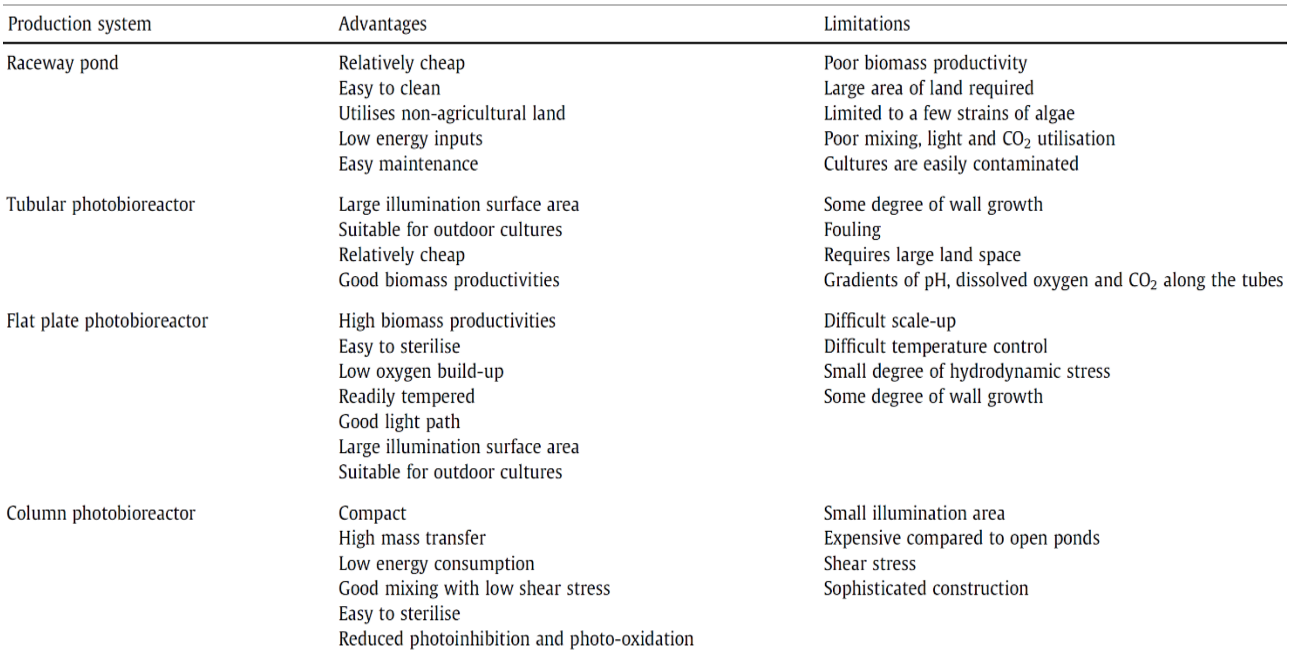
Figure 1.2. Basic design of open pond [11,21] a), and closed photobioreactors [11] b).

Raceway ponds are usually constructed of concrete or plastic. In a continuous production cycle, the nutrients are introduced in front of the paddle wheel and are distributed through the cycle to the extraction point collected. The paddle wheel is in continuous operation to prevent sedimentation. The demand for CO_2 for the microalgae is usually satisfied by contact with the air at the surface, but submersible aerators can be installed to increase the absorption of CO_2.

Closed systems are of different geometries: tubular, flat plate and column photobioreactors. Photobioreactors consist of a series of glass or plastic straight aligned horizontally, vertically, inclined or helical, made of transparent materials to capture the maximum solar energy [21]. The algae are re-circulated with a mechanical pump or an air transport system, to allow gas to be exchanged between the liquid medium and gas aeration, in addition to providing a mixing mechanism [11].

Compared with closed photobioreactors, opened tin is the most economical method of large-scale production of algal biomass. They also have lower energy absorption requirement, and regular maintenance and cleaning are easier and, therefore, may have the potential to return to the production of net energy large [22].

The production of microalgae according to closed photobioreactor technology allowed the culture of single species of microalgae for prolonged durations with a lower risk of contamination [21], and preclude their use for the preparation of high value products for use in the pharmaceutical and cosmetic industries [11]. In figure 1.3 they are listed the advantages and disadvantages for different algal biomass production technologies.



Production system	Advantages	Limitations
Raceway pond	Relatively cheap Easy to clean Utilises non-agricultural land Low energy inputs Easy maintenance	Poor biomass productivity Large area of land required Limited to a few strains of algae Poor mixing, light and CO_2 utilisation Cultures are easily contaminated
Tubular photobioreactor	Large illumination surface area Suitable for outdoor cultures Relatively cheap Good biomass productivities	Some degree of wall growth Fouling Requires large land space Gradients of pH, dissolved oxygen and CO_2 along the tubes
Flat plate photobioreactor	High biomass productivities Easy to sterilise Low oxygen build-up Readily tempered Good light path Large illumination surface area Suitable for outdoor cultures	Difficult scale-up Difficult temperature control Small degree of hydrodynamic stress Some degree of wall growth
Column photobioreactor	Compact High mass transfer Low energy consumption Good mixing with low shear stress Easy to sterilise Reduced photoinhibition and photo-oxidation	Small illumination area Expensive compared to open ponds Shear stress Sophisticated construction

Figure 1.3. Advantages and disadvantages for different of algal biomass production technologies [11].

The open pond systems, require highly selective environments for inherent threat of contamination and pollution from other species of algae and protozoa [23]. Monoculture is possible, by acting on the cultivation, although only a small number of algae are suitable strains.

With regard to the biomass productivity, open pond systems are less efficient than the closed photobioreactors [21]. This can be attributed to several factors, including, the losses by evaporation, temperature variations in the growth media, CO_2 deficiencies, inefficient mixing, and the limitation of light.

In the open pond system, a concentration of biomass of greater than 10 g / l can reach, with extrapolated productivity 25 g / m^2 per day.

1.8 Other applications of microalgae extracts

The human consumption of microalgae is limited to very few species because of the strict food safety rules, commercial factors, market demand and specific preparation. Microalgae can also be used for animal nutrition, for the nutrition of other aquatic species and as a fertilizer for agriculture. It can use the microalgae also for special applications such as the production of proteins, vitamins, polyunsaturated fatty acids, pigments, and other products with high added value. The cultivation of microalgae for pharmaceutical, cosmetic and nutritional already have some importance in the industry but is expected to continue growing in the coming years. The growth of these products is expected as the majority of these substances are currently of synthetic origin, instead of a production from microalgae is considered to be of biological origin. Finally, the most important reason that stimulates the growth of these applications is the economic value that these have on the market. The price of beta-carotene for example, can also exceed 2000 Euros per kilogram of product, while that of astaxanthin reaches 7000 Euros per kilogram [11].

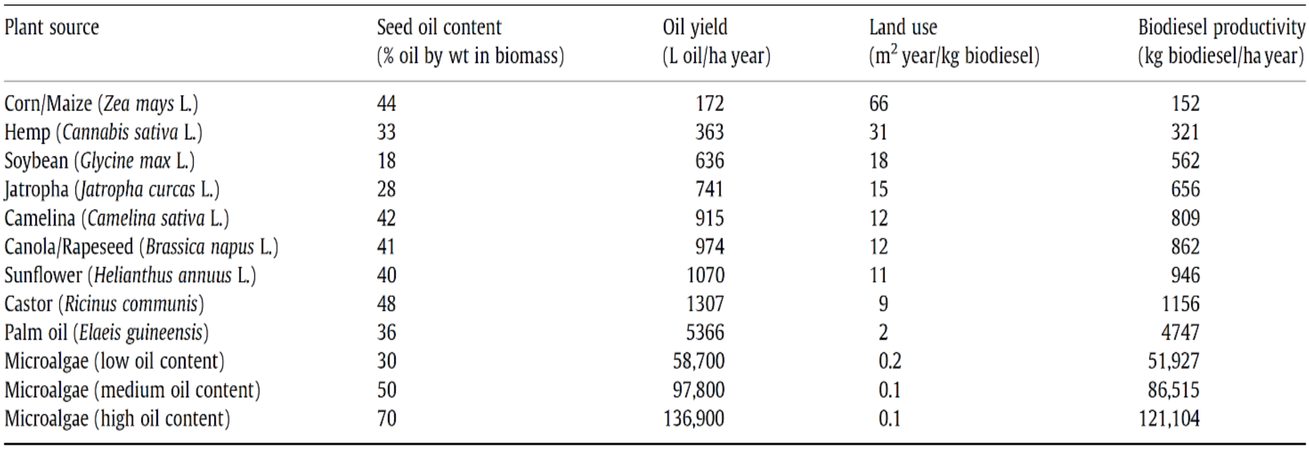
The difficulties related to the production of co-products from microalgae is in the fact that the species must be selected and cultivated under specific conditions, also the amount of contained substances is very low compared to the total biomass. The selection of strains, cultivation technologies, recollection and especially extraction of these products are still developing.

Evidence that the concurrent extraction of valuable co-products with biofuel production has significant potential. Therefore, large-scale production of microalgae for biofuels will increase the availability of these products [11].

1.9 Productivity of lipids

Many strains of microalgae naturally have a high content of lipids (about 20-50% dry weight), but it is possible to increase the concentration by optimizing the growth determinants, such as controlling the level of nitrogen [24], light intensity, temperature and salinity [25], the concentration of CO_2 [26] and the collection procedure [24]. However, increasing the accumulation of lipids will not result in an increase in productivity of lipids, as the productivity of biomass and accumulation of lipids are not necessarily related [27]. The accumulation of lipid refers to an increase in the concentration of lipids within the cells of microalgae without taking into account the overall biomass production. The productivity of lipids takes into account both the concentration of lipids within the cells and the biomass produced by these cells and is therefore a more useful indicator of the potential of liquid biofuels production costs [11].

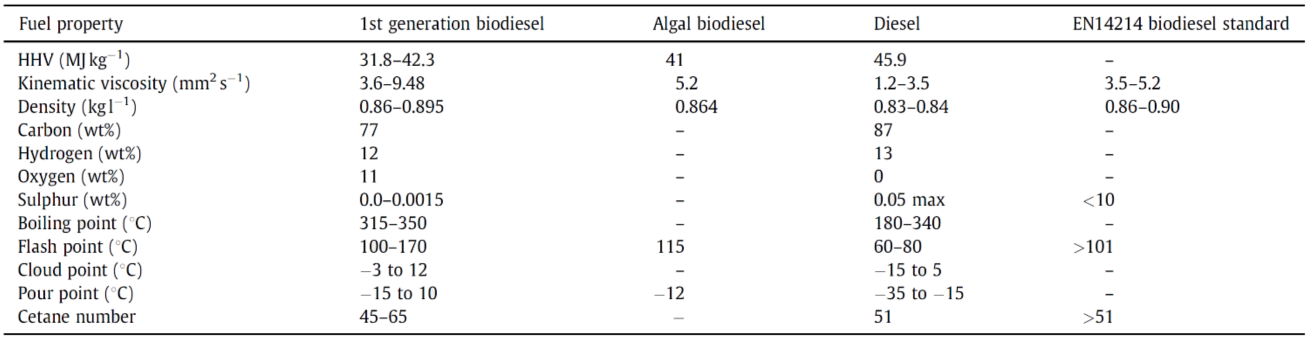
The most effective method to improve microalgae lipid accumulation is nitrogen limitation, resulting not only in the accumulation of lipids, but also results in a gradual change of the composition of triglycerides (TG) [24]. In nitrogen deficiency, cell proliferation is prevented, but carbon is still assimilated by the cell and converted to lipids that are stored in the existing cells thereby increasing the concentration [24]. Microalgae have the highest yield of oil between oily species. They are able to produce from 60000 to more than 130000 liters of oil per hectare per year, while terrestrial plants like palm, castor, sunflower and rapeseed produce up to 5366, 1307, 1070 and 974 liters per hectare per year, respectively. A comparison between the oil yield of microalgae and some terrestrial plants is shown in Figure 1.4 [28]. The figure also shows the percentage of lipids with respect to the dry mass units, and the area required for the cultivation.



Plant source	Seed oil content (% oil by wt in biomass)	Oil yield (L oil/ha year)	Land use (m^2 year/kg biodiesel)	Biodiesel productivity (kg biodiesel/ha year)
Corn/Maize (*Zea mays* L.)	44	172	66	152
Hemp (*Cannabis sativa* L.)	33	363	31	321
Soybean (*Glycine max* L.)	18	636	18	562
Jatropha (*Jatropha curcas* L.)	28	741	15	656
Camelina (*Camelina sativa* L.)	42	915	12	809
Canola/Rapeseed (*Brassica napus* L.)	41	974	12	862
Sunflower (*Helianthus annuus* L.)	40	1070	11	946
Castor (*Ricinus communis*)	48	1307	9	1156
Palm oil (*Elaeis guineensis*)	36	5366	2	4747
Microalgae (low oil content)	30	58,700	0.2	51,927
Microalgae (medium oil content)	50	97,800	0.1	86,515
Microalgae (high oil content)	70	136,900	0.1	121,104

Figure 1.4. Comparison of microalgae with other oil crops [28].

Algal biodiesel can be an accepted substitution of the fossil diesel only if its properties match the International Biodiesel Standard for Vehicles (EN14214). Algal oils contain a high degree of polyunsaturated fatty acids when compared to vegetable oils, which makes it susceptible to oxidation in storage and therefore limits utilisation [11]. Algal biodiesel has similar physical and chemical properties than petroleum diesel (figure 1.5).



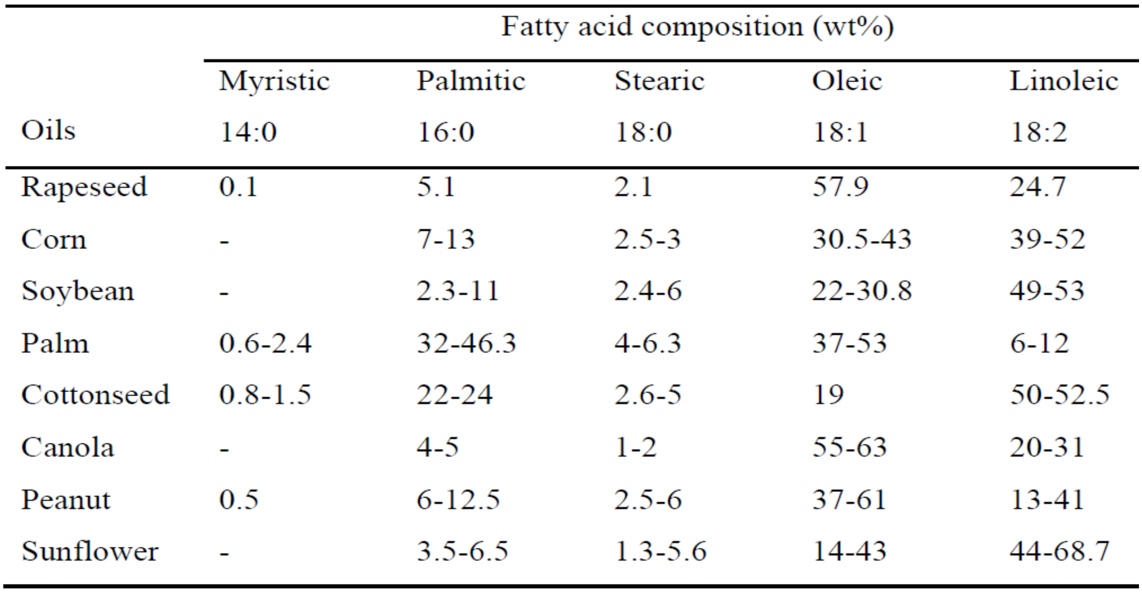
Fuel property	1st generation biodiesel	Algal biodiesel	Diesel	EN14214 biodiesel standard
HHV (MJ kg^{-1})	31.8–42.3	41	45.9	–
Kinematic viscosity ($mm^2 s^{-1}$)	3.6–9.48	5.2	1.2–3.5	3.5–5.2
Density ($kg l^{-1}$)	0.86–0.895	0.864	0.83–0.84	0.86–0.90
Carbon (wt%)	77	–	87	–
Hydrogen (wt%)	12	–	13	–
Oxygen (wt%)	11	–	0	–
Sulphur (wt%)	0.0–0.0015	–	0.05 max	<10
Boiling point (°C)	315–350	–	180–340	–
Flash point (°C)	100–170	115	60–80	>101
Cloud point (°C)	−3 to 12	–	−15 to 5	–
Pour point (°C)	−15 to 10	−12	−35 to −15	–
Cetane number	45–65	–	51	>51

Figure 1.5. Comparison of properties of 1st generation biodiesel, microalgae oil and fossil fuel [11].

1.10 Triglyceride feedstocks and reaction pathways

Vegetable oil has gained significant interest as sustainable source of biofuel because of their high energy density and structural similarity to petroleum-based fuels of the product that can be obtained from their processing. The composition of vegetable oil feeds depends largely on their origin, but in general, these feeds consist of triglycerides comprising various saturated and unsaturated fatty acids [29].

The chemical composition of an oil is expressed by the percentage by weight of constituent free fatty acid chains in the triglycerides. Typically, the oil also contain small fractions of free fatty acids, the extent of which depends on the particular source. Free fatty acids are characterized by the. A typical composition of base oil plants is represented in figure 1.6 where notation m:n below the name of the acid respectively indicate the number of carbons and double bonds present in the hydrocarbon skeleton of the glycerol ester considering that it is formally generated by esterification reaction of fatty acid and glycerin. The oil obtained from microalgae strongly depends on the cultivated species and the growing conditions, so it is not possible to give a composition representative of all the oils. In general, from microalgae one can get all types of fatty acids found in the living species.



	Fatty acid composition (wt%)				
	Myristic	Palmitic	Stearic	Oleic	Linoleic
Oils	14:0	16:0	18:0	18:1	18:2
Rapeseed	0.1	5.1	2.1	57.9	24.7
Corn	-	7-13	2.5-3	30.5-43	39-52
Soybean	-	2.3-11	2.4-6	22-30.8	49-53
Palm	0.6-2.4	32-46.3	4-6.3	37-53	6-12
Cottonseed	0.8-1.5	22-24	2.6-5	19	50-52.5
Canola	-	4-5	1-2	55-63	20-31
Peanut	0.5	6-12.5	2.5-6	37-61	13-41
Sunflower	-	3.5-6.5	1.3-5.6	14-43	44-68.7

Figure 1.6. Fatty acid composition of vegetable oils [30]. The nomenclature shows the number of carbon atoms and the number of double bonds.

Since the vegetable oil is not directly suitable as biofuel, several upgrading processes have been developed over the years to produce renewable diesel that can be used in modern engine. These processes can be divided into three categories: cracking, transesterification, and deoxygenation [29,31]. In Figure 1.7 are summarized the processes used for transformation of oils into biofuels.

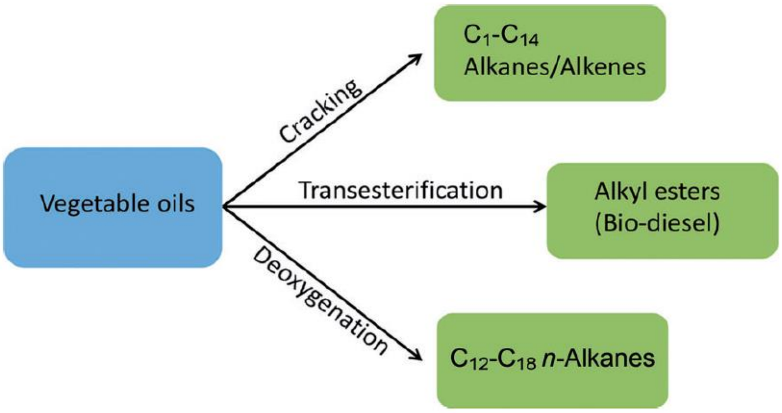


Figure 1.7. The possible ways of transforming vegetable oils into biofuels [29].

Cracking is based on the thermal or thermos-catalytic decomposition of triglycerides in lighter products among which alkanes, alkenes, and fatty acids are included [32]. Conventional cracking catalysts used in the petrochemical industry, that is, zeolites and mesoporous aluminosilicates, can also be applied to vegetable oils [32]. The process is, however, slightly selective because a large range of hydrocarbons and oxygenates are formed [32]. Therefore, cracking is not the optimal upgrading technology of vegetable oils for the production of diesel-type biofuels.

Transesterification is currently the major process that is commercially applied to produce biodiesel from vegetable oils. The resulting fatty acid methyl esters (FAMEs) or fatty acid ethyl esters (FAEEs) are, however, not fully compatible with conventional diesel engines owing to the still relatively high oxygen content of fatty acid esters. As a result, this type of biodiesel has to be blended with petroleum fuel or engines have to be adapted [33]. Other disadvantages of FAMEs are poor cold-flow properties because of the high cloud point, pour point, and cold filter plugging point. One of the major disadvantages of homogeneous catalysts in transesterification is that they are difficult to be reused or regenerated, because separation of catalyst from products is difficult and requires more equipment which could result in higher production costs [32,34]. Besides, the process is not environmentally friendly because a large amount of waste water is produced in the separation step. Developing a new solid catalyst seems to be an appropriate solution to overcome problems associated with homogeneous catalysts. The heterogeneous catalysts can be easily separated from the products that do not contain impurities of the catalyst and the cost of final separation could be reduced. Moreover the catalysts can also be readily regenerated and reused and it is more environmentally benign because there is no need of neutralization and there are less problem of waste treatment [35]. Nevertheless, one of the major problems associated with transesterification of vegetable oils with heterogeneous catalysts is the formation of a three phase reaction system with alcohol and oil which leads to diffusion limitations thus lowering the rate of the reaction [36].

Most concerns regarding biodiesel can be overcome by lowering its oxygen content using suitable heterogeneous catalysts. This can be achieved by catalytic deoxygenation process. The resulting not oxygenated hydrocarbons are compatible with fossil fuels and with conventional diesel engines. Catalytic deoxygenation of vegetable oils can also be used for the production of bulk chemicals. These chemicals could, for instance, be produced by promoting selectivity of deoxygenation toward the production of linear olefins. The use of vegetable oil-based feedstocks for the production of linear olefins has raised interest because of their higher added value compared to fuels since they are interesting building blocks for the production of surfactants and lubricants [37]. Moreover short-chain linear olefins are used as co-monomers in the production of linear low-density polyethylene. Thus, vegetable oil-based feeds can be regarded as an interesting source for the production of both fuels and chemicals.

Nowadays, most processes for the catalytic deoxygenation of vegetable oil are hydro-processes and thus require H_2. A potential disadvantage of this process is the availability of H_2, which is still mostly produced from non-renewable feedstocks.

The possibility of eliminating oxygen with heterogeneous catalysts from fatty acids and esters under inert gas has gained a lot of attention [38]. Recently, the use of special solvents for the reaction of catalytic deoxygenation has been the subject of study for researchers. Water at high temperature and pressure seems to attract much interest for its capacity to solubilize even hydrophobic organic compounds. In addition, the water may also favour the production of hydrogen by the decomposition of glycerol generated by hydrolysis of TG and the water-gas-shift reaction [39]. The thermal treatment of oils in water has many advantages including the in situ production of hydrogen, the use of a readily separable ecological solvent. The process could be useful from both the environmental and economic point of view.

Most of deoxygenation studies have been performed on model compounds rather than on triglyceride feedstocks. Fatty acids, fatty acid esters, and specific triglycerides are mostly studied because of their structural similarity to vegetable oils and are, therefore, often regarded as suitable model compounds.

1.11 Scope of this thesis

Purpose of this thesis work was to study the production of biofuels through the use of thermo-catalytic conversion processes of vegetable oils. The vegetable oil was converted into biodiesel through the transesterification and interesterification processes using new heterogeneous catalysts based on tin. The interesterification is a particular process to transform oil into biofuel that has some advantages compared to the transesterification process avoiding the formation of glycerol. In this case in fact the biodiesel co-product is triacetin, a compound with added value higher than glycerol, and with chemical-physical characteristics that allow its use in the biodiesel as an additive.

Further processes that have been studied to obtain liquid and gaseous hydrocarbons are based on the hydrothermal deoxygenation of fatty acids and glycerol in the presence of solid catalysts. The hydrothermal treatment of triglycerides was studied considering that glycerol could be a valuable source of hydrogen, rather than a co-product.

The hydrothermal deoxygenation experiments were initially carried out in batch reactors. Heterogeneous catalysts based on nickel have proven to be a viable alternative to more expensive catalysts based on noble metals. A continuous laboratory plant has been also realized in order to carry out the hydrothermal processes at high temperature on oils or on model compounds. The plant is also able to work in operative conditions suitable to have water at its supercritical condition and has been designed to study the conversion of vegetable oils into biofuels in aqueous reaction system. The tubular reactor can be filled with solid catalysts to form a catalytic fixed bed.

Each topic mentioned previously has been addressed and presented by devoting it a chapter of this thesis. In the second chapter the transesterification process of rapeseed oil with methanol in the presence of a tin-based heterogeneous catalyst has been studied. In the third chapter the same catalyst was used for the interesterification of rapeseed oil with methyl acetate. The most important parameters controlling the process of biodiesel production have been investigated and discussed for both technologies. In addition, some investigations have been carried out for the characterization of the solid catalyst.

The fourth chapter has been devoted to the study of processes of hydrothermal deoxygenation of fatty acids and gasification of glycerol, used as model compounds in the presence of catalysts based on nickel. The water was used as reaction medium in conditions close to the critical point (T_c = 375 °C and P_c = 221 bar), but it has been shown that it may also participate in the chemical reactions with the role of reagent.

Finally, the fifth chapter contains the description of a laboratory scale continuous plant realized for the purpose of study the gasification reactions in supercritical water of organic compounds. The continuous system allows to treat real biomass or model compounds at temperatures up to 550 °C, both in the absence of catalyst and in the presence of a heterogeneous catalyst confined inside the reactor. Some preliminary testing on non-catalytic gasification in supercritical water have been carried out and presented.

REFERENCE

[1] Goncalves, A. L.; Pires, J. C. M.; Simoes, M. Green fuel production: processes applied to microalgae. Environ. Chem. Lett. 11, 2013, 315–324.

[2] Bensaid, S.; Centi, G.; Garrone, E.; Perathoner, S; Saracco G. Towards Artificial Leaves for Solar Hydrogen and Fuels from Carbon Dioxide, Chem. Sus. Chem. 5, 2012, 500 – 521.

[3] Rittmann, B. E. Opportunities for Renewable Bioenergy Using Microorganisms Biotechnology and Bioengineering, 100, 2008, 203-212.

[4] Goldemberg J, Johansson TB. World Energy Assessment Overview: 2004 Update. New York: United Nations Development Programme.

[5] Masters G.M.; Ela W.P. Introduction to environmental engineering and science. 3rd edn. 2008. Upper Saddle River, NJ: Prentice-Hall.

[6] IPCC, Summary for policymakers, in Climate Change 2007: The Physical Science Basis: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, S. Solomon et al., Eds. (Cambridge Univ. Press, New York, 2007).

[7] UNDP (2007) Human development report 2007/2008. Fighting climate change: human solidarity in a divided world. United Nations Development Programme, NY.

[8] Hall DO, Rosillo-Calle F. 1998. Biomass resources other than wood. London: World Energy Council.

[9] Carrol J, Parker M. 2007. Ethanol producers rethink investment. Detroit Free Press. 25 November 2007.

[10] Giampietro M, Mayumi K. 2007. Checking the quality of primary energy sources: Why we believe that the idea of large-scale production of biofuels from agricultural land is a hoax. Proc. 9th Biennial Conf. Intl. Society of Ecol. Econ., 2006, 16–18.

[11] Brennan, Owende, L. P. Biofuels from microalgae-A review of technologies for production, processing, and extractions of biofuels and co-products. Renewable and Sustainable Energy Reviews 14, 2010, 557–577.

[12] National Research Council (NRC) Committee on Water Implications of Biofuels Production in the United States. 2007. Water implications of biofuels production in the United States. Washington, DC: National Academy Press.

[13] Energy Information Administration. 2005. Annual Energy Outlook: With Projection to 2030. U.S. Department of Energy, Washington, DC.

[14] Sirajunnisa, A. R., Surendhiran, D. Algae – A quintessential and positive resource of bioethanol production: A comprehensive review, Renewable and Sustainable Energy Reviews 66, 2016, 248–267.

[15] Wang B, Li Y, Wu N, Lan C. CO2 bio-mitigation using microalgae. Applied Microbiology and Biotechnology 79(5): 2008, 707–18.

[16] Ono E, Cuello JL. Feasibility assessment of microalgal carbon dioxide sequestration technology with photobioreactor and solar collector. Biosystems Engineering 95(4):2006; 597–606.

[17] Pulz O, Scheinbenbogan K. Photobioreactors: design and performance with respect to light energy input. Advances in Biochemical Engineering/Biotechnology 59:1998; 123–52.

[18] Suh IS, Lee CG. Photobioreactor engineering: design and performance. Biotechnology and Bioprocess Engineering 8(6):2003, 313–21.

[19] Welsh DT, Bartoli M, Nizzoli D, Castaldelli G, Riou SA, Viaroli P. Denitrification, nitrogen fixation, community primary productivity and inorganic-N and oxygen fluxes in an intertidal Zostera noltii meadow. Marine Ecology Progress Series 208:2000; 65–77.

[20] Hsieh C-H, Wu W-T. Cultivation of microalgae for oil production with a cultivation strategy of urea limitation. Bioresource Technology 100 (17):2009, 3921–6.

[21] Chisti Y. Biodiesel from microalgae. Biotechnology Advances 25(3):2007, 294–306.

[22] Rodolfi L, Zittelli GC, Bassi N, Padovani G, Biondi N, Bonini G, et al. Microalgae for oil: strain selection, induction of lipid synthesis and outdoor mass cultivation in a low-cost photobioreactor. Biotechnology and Bioengineering 2008, 102(1):100–12.

[23] Pulz O, Scheinbenbogan K. Photobioreactors: design and performance with respect to light energy input. Advances in Biochemical Engineering/Biotechnology 1998, 59:123–52.

[24] Widjaja A, Chien C-C, Ju Y-H. Study of increasing lipid production from fresh water microalgae Chlorella vulgaris. Journal of the Taiwan Institute of Chemical Engineers 2009, 40(1):13–20.

[25] Qin J. Bio-hydrocarbons from algae impacts of temperature, light and salinity on algae growth. Barton, Australia: Rural Industries Research and Development Corporation, 2005.

[26] de Morais MG, Costa JAV. Isolation and selection of microalgae from coal fired thermoelectric power plant for biofixation of carbon dioxide. Energy Conversion and Management 2007;48(7):2169–73.

[27] Sheehan J, Dunahay T, Benemann JR, Roessler P. A look back a U.S. Department of Energy's Aquatic Species Program—biodiesel from algae. U.S. Department of Energy; 1998.

[28] Mata, T. M. Martins, A. A. Caetano, N. S. Microalgae for biodiesel production and other applications: A review. Renewable and Sustainable Energy Reviews 14(1), 2010, 217–232.

[29] Gosselink, R. W. Hollak, S. A. W. Chang, S.W. Haveren, J. Jong, K.P. Bitter, J. H., Es, D. S. Reaction Pathways for the Deoxygenation of Vegetable Oils and Related Model Compounds Chem.Sus.Chem. 6, 2013, 1576 – 1594.

[30] G. Knothe, Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters, Fuel Process. Technol. 86, 2005, 1059.

[31] Lestari, S. Maki-Arvela, P. Beltramini, J. Lu, G. Q. M. Murzin, D. Y. Transforming Triglycerides and Fatty Acids into Biofuels, Chem-Sus.Chem. 2009, 2, 1109– 1119.

[32] M.Snre, P. Mki-Arvela, I. L. Simakova, J. Myllyoja, D. Y. Murzin, Overview of catalytic methods for production of next generation biodiesel from natural oils and fats, Russ. J. Phys. Chem. B 2009, 3, 1035 –1043.

[33] B. Smith, H. C. Greenwell, A. Whiting, Catalytic upgrading of tri-glycerides and fatty acids to transport biofuels, Energy Environ. Sci. 2009, 2, 262 – 271.

[34] Activity of solid catalysts for biodiesel production: A review Masoud Zabeti, Wan Mohd Ashri Wan Daud, Mohamed Kheireddine Aroua.

[35] T.F. Dossin, M.-F. Reyniers, R.J. Berger, G.B. Marin, Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production, Applied Catalysis B 67 (2006) 136–148.

[36] I.K. Mbaraka, B.H. Shanks, Conversion of oils and fats using advanced mesoporous heterogeneous catalysts, JAOCS Journal of the American Oil Chemists' Society 83 (2006) 79–91.

[37] F. van der Klis, J. Le Ntre, R. Blaauw, J. van Haveren, D. S. van Es, Renewable linear alpha olefins by selective ethenolysis of decarboxylated unsaturated fatty acids, Eur. J. Lipid Sci. Technol. 2012, 114, 911– 918.

[38] E. Santillan-Jimenez, M. Crocker, Catalytic deoxygenation of fatty acids and their derivatives to hydrocarbon fuels via decarboxylation/decarbonylation, 87(8), 2012, 1041–1050.

[39] S. A. W. Hollak, M. A. Arins, K. P. de Jong, D. S. van Es. Hydrothermal Deoxygenation of Triglycerides over Pd/C aided by In Situ Hydrogen Production from Glycerol Reforming, 7(4), 2014, 1057–1062.

Chapter 2

BIODIESEL PRODUCTION USING TRANSESTERIFICATION REACTION

2.1 Introduction

Transesterification, called also alcoholysis, is the reaction of triglyceride with short-chain alcohol, commonly methanol, in the presence of suitable basic or acid catalysts. The transesterification of triglycerides for biodiesel production could be described as in figure 2.1:

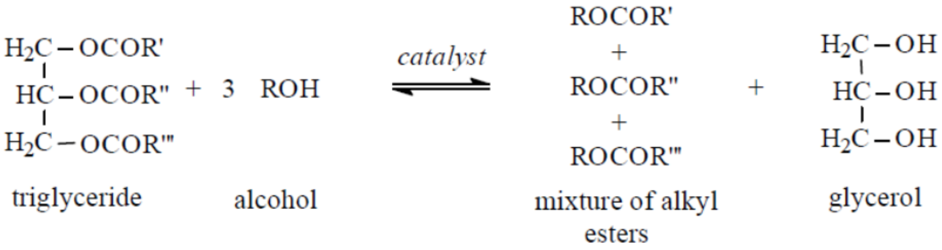


Figure 2.1. Transesterification of vegetable oils.

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters (i.e. biodiesel) and glycerol. Alcohol and oil form two distinct phases, and therefore the reaction occurs at the interface. To promote the transport of matter between the two phases is practiced a vigorous stirring during the reaction. At the end of the process are obtained again two phases: an alcohol containing glycerol and non-reacted alcohol and oil-rich phase containing the mixture of alkyl esters. Stoichiometrically, one mole of triglyceride reacts with three moles of alcohol, but to achieve a high yield of the esters, the alcohol has to be used in excess. The transesterification is an equilibrium reaction and the transformation can also activated thermally by mixing the reactants at high enough temperature in the presence of the supercritical alcohol. However, the presence of a catalyst accelerates considerably the achievement of the equilibrium and allows to work at lower temperature. The transesterification reaction can be catalysed by acids and bases dissolved in the alcohol phase (homogeneous catalysis) or acidic and basic species present on solid surfaces (heterogeneous catalysis). Some techniques such as the use of ultrasound and microwaves can promote the kinetics of the transesterification reaction. The process can also be catalysed by enzymes [1].

2.2 Homogeneous acid-catalysed transesterification

The transesterification process is catalysed by Bronsted or Lewis acids, preferably by sulfonic and sulfuric acids. The mechanism of the acid-catalysed transesterification for a monoglyceride is shown in figure 2.2, but it can be extended to di- and triglycerides. It is generally accepted that the protonation of the carbonyl group of the ester leads to the formation of carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+ [2].

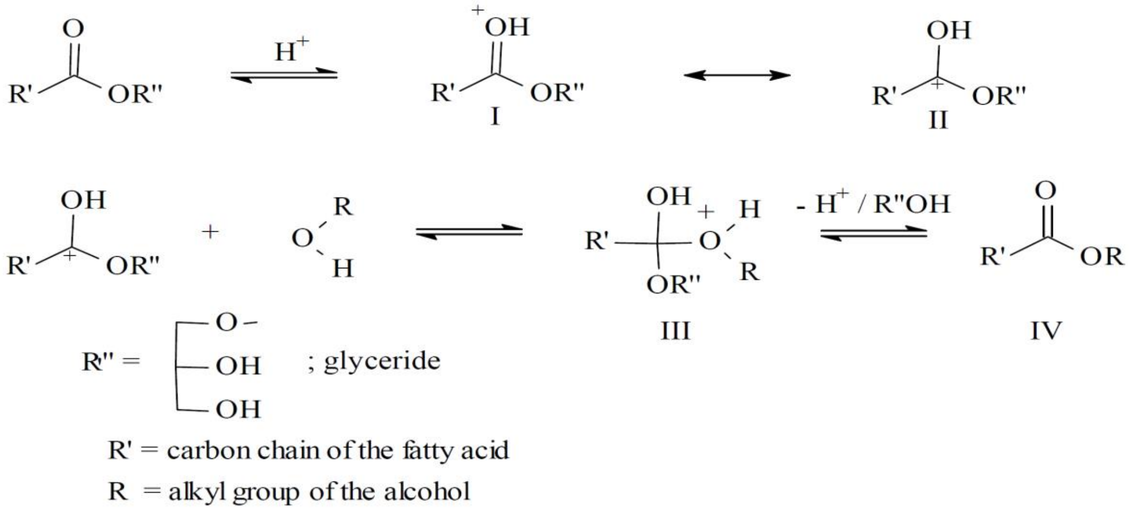


Figure 2.2. Mechanism of the transesterification of vegetable oils catalysed by acid.

In order to obtain good biodiesel yields in reasonable reaction times, acid-catalysed transesterification is generally carried out at high alcohol-to-oil molar ratios, higher temperatures and catalyst concentrations with respect to the same process activated by base catalysts. In fact, the homogeneous acid-catalysed reaction is about 4000 times slower than the homogeneous base-catalysed reaction [3]. The acid-catalysed transesterification should be carried out in the absence of water so that high yields in alkyl esters require temperatures above 100 °C and more than 3 h of reaction time [3].

The reaction of acid-catalysed transesterification has an important advantage compared with that catalysed by base, namely the ability to convert to free fatty acids (FFAs) into biodiesel. Any FFAs present in feedstock, in the presence of alcohol and the acid catalyst are converted into esters by the reaction of esterification. The esterification reaction is represented in Figure 2.3:

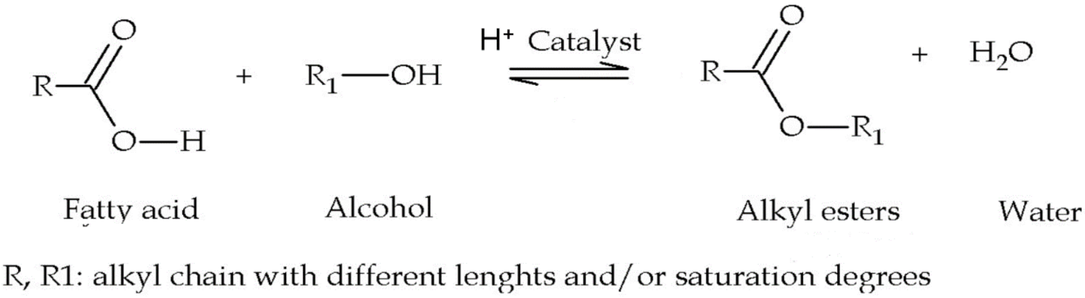


Figure 2.3. Esterification in acid catalyst reaction to convert FFA to biodiesel.

The acid-catalyzed transesterification is very useful to process waste oils or fats with high FFAs content (for example waste cooking oil), because acid catalysts can simultaneously catalyse both transesterification and esterification of FFA. The reaction of esterification of FFA not directly impacts on the overall performance of the production of biodiesel, but the water that is formed as a coproduct cause problems. The negative impact of water on acid catalysis is caused by the fact that the water can solvate the protons deactivating the acid catalyst. A study of the acid-catalysed transesterification shows that a concentration 0.1 % w/w of water (oil-based), is able to influence the yield of esters, while a concentration of 5 % w/w can completely inhibit the reaction. The authors used a molar methanol to oil ratio 6:1, a temperature of 60 ° C, a reaction time of 96 hours and 3% w/w of sulfuric acid as catalyst [4]. The concentration of FFA in feedstock must be so limited due to the production of water from the esterification reaction (Figure 2.3). The authors in the same operating conditions have also studied the effect of the concentration of FFA on the yield of esters. They found that in the conditions adopted in the concentration must be kept always less than 5% w/w to obtain yields esters higher than 90%.

2.3 Homogeneous base-catalyzed transesterification

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalysed reaction [3]. Due to this reason, together with the fact that the alkaline catalysts are less corrosives than acidic compounds, industrial processes usually favour base catalysts, such as sodium or potassium hydroxide [3].

Industrially the production of biodiesel through homogeneous basic catalysis is conducted at a temperature close to the boiling point of the alcohol used (60-65 ° C when methanol is used), a molar ratio of oil to alcohol of about 6:1 and a concentration of catalyst 0.5-2 % w/w. (oil basis). In these conditions, the pressure is equal to the vapor pressure of the alcohol (1-4 bars) and after about 1 hour of treatment it is possible to obtain conversions higher than 98% [6].

In figure 2.4 it is shown the generally accepted mechanism of the transesterification reaction catalysed by basic compounds [2]. The first step (1) produces an alkoxide and the protonated catalyst. In the second step (2) the alkoxide brings a nucleophilic attack to the carbonyl group of the triglyceride and a tetrahedral intermediate is generated. In the third step (3), the alkyl ester and the corresponding anion of the diglyceride are formed [2].

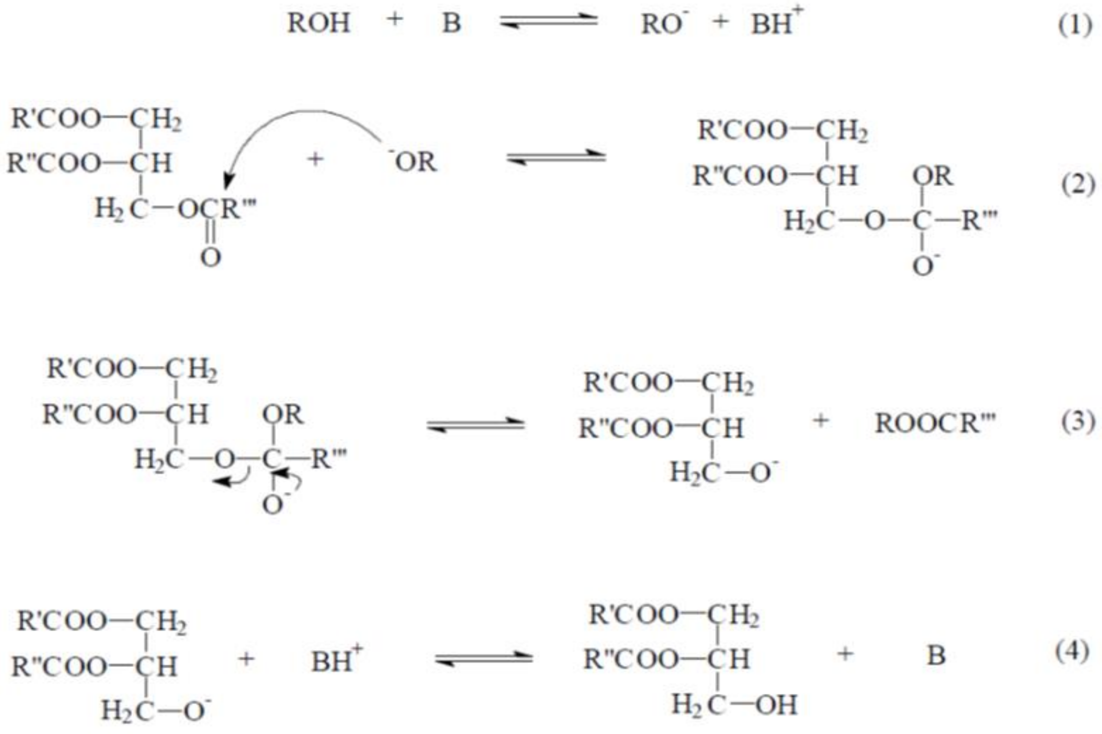


Figure 2.4. Mechanism of the transesterification of vegetable oils catalysed by basic.

The latter (3) deprotonates the catalyst, thus regenerating the active species. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

Alkaline metal alkoxides (as CH_3ONa) are the most active catalysts, alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversion by increasing the catalyst concentration. Even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol [2]. Water is undesired chemical species for the base-catalyzed transesterification reaction because due to the hydrolysis of the ester alkyl with consequent formation of FFA (Figure 2.5).

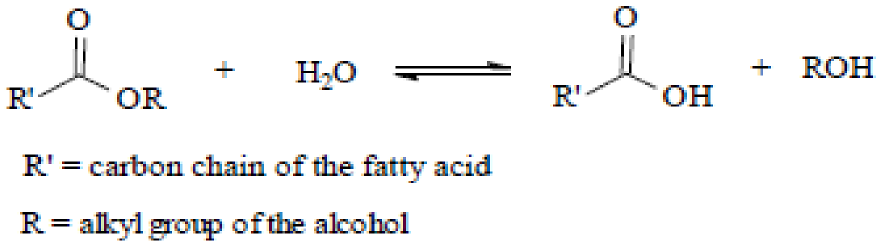


Figure 2.5. Hydrolysis alkyl ester to form FFA and alcohol.

This not only involves a decrease in the yield of esters, also triggers the saponification reaction, which consists in the reaction of FFA with the metal hydroxide which then is consumed (Figure 2.6).

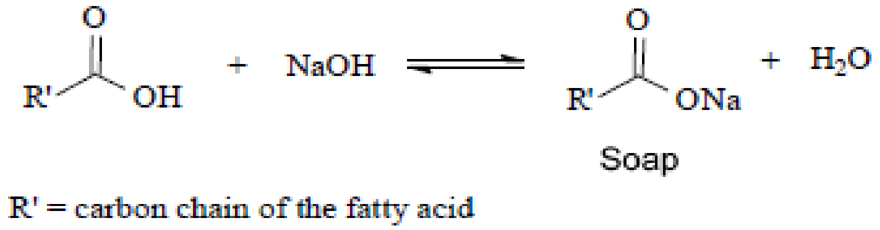


Figure 2.6. Soap formation reaction by free fatty acid.

Furthermore, the water obtained from the saponification reaction is available to hydrolyze another ester molecule and begin again the cycle of unwanted reactions until equilibrium is reached. The soap increases the viscosity of the reaction mixture and causes the formation of stable emulsions, hindering the separation of the products [3].

To make the process economically viable is therefore necessary to pre-treat the reactant mixture so as to totally eliminate the water content or keep it below 0.3% w/w. The treatment of the reagents must also provide for the eventual elimination or reduction of FFAs, which must not exceed 0.5% w/w. [5].

2.4 Heterogeneous acid-catalyzed transesterification

Despite industrially homogeneous catalysis is the most used, it has some drawbacks that impact the global economy of the process. The cost of biodiesel produced in fact, is not yet competitive with fossil fuel, mainly caused by the high cost of the raw material used. Moreover, in homogeneous catalysis at the end of the reaction it is necessary to neutralize the catalyst that thus cannot be reused. The neutralization step also generates polluting effluents, which causes problems of environmental impact. The total cost of the biodiesel production process using homogeneous catalysis is also complicated by the use of highly corrosive liquids towards the equipment materials (strong acids and bases). The transesterification process with solid catalysts presents interesting advantages that could lead to lower overall costs and a more respectful process for the environment [7]. The solid catalysts do not require neutralization at the end of the test and can be separated very easily from the liquid phase. Consequently, it is possible to reuse the catalyst and avoids the production of waste and the use of corrosive liquids.

Moreover, the solid catalyst appears to be more resistant to the presence of water and free fatty acids in the raw material and therefore can be also used for waste oil or unrefined [8]. Finally, the solid catalyst also allows to operate in continuous processes simply realizing a fixed bed inside a reactor. All these benefits can help make the solid transesterification process catalysed a potentially cheaper alternative to conventional processes.

However, the heterogeneous catalysis still has some limitations mainly related to the low speed of the reaction. The kinetics of the transesterification reaction in general is slowed by the presence of the two phases (alcoholic and oily): the presence of the heterogeneous catalyst constitutes a third distinct phase that complicates the transport of matter. For this reason, the kinetics of the transesterification reaction is slower than that homogeneous. The ideal solid acid catalyst should have a high surface area and a pore size such as to allow the diffusion of reactants and products, a high concentration of active sites and a high resistance to the presence of impurities.

The solid acid catalysts are able to catalyse the esterification reaction and transesterification simultaneously and thus are suitable for treatment of oils with a high content of FFAs. The catalytic sites can be either Bronsted acids that Lewis acids. In particular, the Bronsted acids, have the great advantage of promoting the esterification reaction, but are less active compared to Lewis acids. The Lewis acids are more active for the transesterification reaction but are also more susceptible to poisoning. To avoid the deactivation caused by water the surface of the catalyst must be hydrophobic. An ideal catalyst acid must therefore be bifunctional in order to exploit the advantages of both types of acidity. The solid catalysts most studied in the literature acids are sulfated ZrO_2, sulfated TiO_2, SnO_2 sulfated, among Bronsted acids, and zirconium oxide, titanium oxide, tin oxide and niobium oxide (ZrO_2, TiO_2, SnO_2, NbO_2) among Lewis acids.

The reaction mechanism of an acid heterogeneous catalyst is show in figure 2.7.

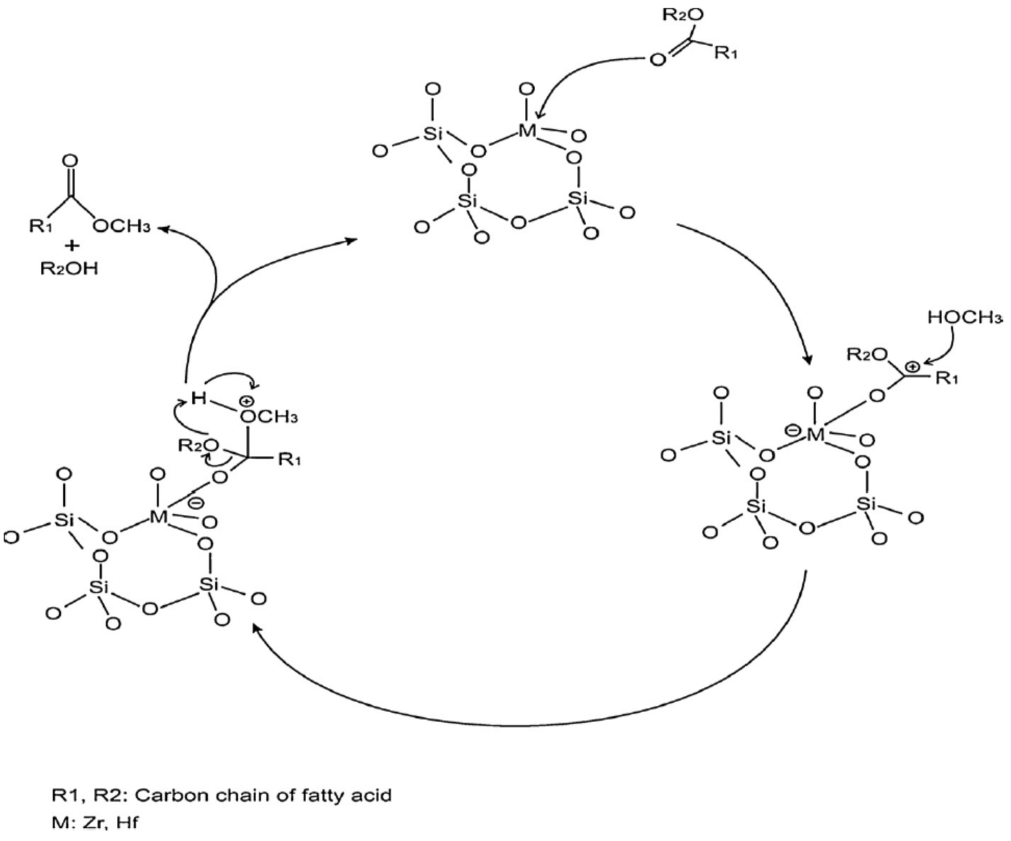
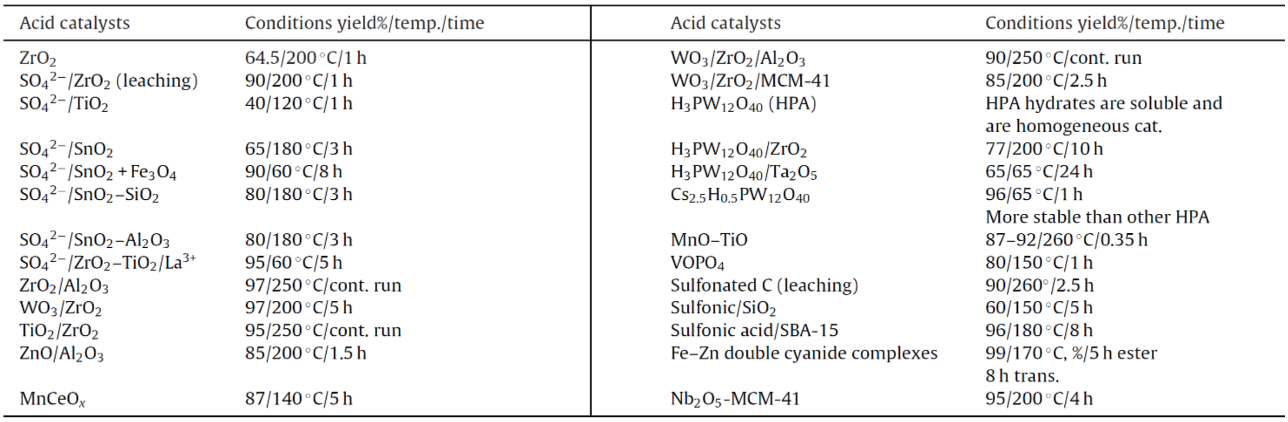


Figure 2.7. Chemical mechanism of an acid heterogeneous catalyst: MeO_2 supported on SiO_2 [8].

Figure 2.8 shows some catalysts used, the yields obtained and the operating conditions adopted. It should be noted that with these catalysts, the reaction must be conducted at significantly higher temperatures than homogeneous catalysis.



Acid catalysts	Conditions yield%/temp./time	Acid catalysts	Conditions yield%/temp./time
ZrO_2	64.5/200 °C/1 h	$WO_3/ZrO_2/Al_2O_3$	90/250 °C/cont. run
SO_4^{2-}/ZrO_2 (leaching)	90/200 °C/1 h	WO_3/ZrO_2/MCM-41	85/200 °C/2.5 h
SO_4^{2-}/TiO_2	40/120 °C/1 h	$H_3PW_{12}O_{40}$ (HPA)	HPA hydrates are soluble and are homogeneous cat.
SO_4^{2-}/SnO_2	65/180 °C/3 h	$H_3PW_{12}O_{40}/ZrO_2$	77/200 °C/10 h
$SO_4^{2-}/SnO_2 + Fe_3O_4$	90/60 °C/8 h	$H_3PW_{12}O_{40}/Ta_2O_5$	65/65 °C/24 h
$SO_4^{2-}/SnO_2–SiO_2$	80/180 °C/3 h	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	96/65 °C/1 h More stable than other HPA
$SO_4^{2-}/SnO_2–Al_2O_3$	80/180 °C/3 h	MnO–TiO	87–92/260 °C/0.35 h
$SO_4^{2-}/ZrO_2–TiO_2/La^{3+}$	95/60 °C/5 h	$VOPO_4$	80/150 °C/1 h
ZrO_2/Al_2O_3	97/250 °C/cont. run	Sulfonated C (leaching)	90/260°/2.5 h
WO_3/ZrO_2	97/200 °C/5 h	Sulfonic/SiO_2	60/150 °C/5 h
TiO_2/ZrO_2	95/250 °C/cont. run	Sulfonic acid/SBA-15	96/180 °C/8 h
ZnO/Al_2O_3	85/200 °C/1.5 h	Fe–Zn double cyanide complexes	99/170 °C, %/5 h ester 8 h trans.
$MnCeO_x$	87/140 °C/5 h	Nb_2O_5-MCM-41	95/200 °C/4 h

Figure 2.8. Heterogeneous acid catalysts, for the transesterification reaction, studied in the literature [11].

Other interesting acid heterogeneous catalysts are ion exchange resins which, however, have a polymer matrix and cannot be used at high temperatures. The resins allow easily to modulate the number of catalytic sites, surface area, the pore size and the hydrophobicity of the catalyst [9].

The heteropolyacids are another interesting category of acid catalysts with flexible structure and with the capacity to produce super-acidity [12]. The heteropolyacids are structures constituted by metal oxides (generally the metal is W, Mo or V) that form a cluster within which is located an oxide of a heteroatom (the heteroatom may be Si, P or As). These structures are soluble in the polar and therefore must be supported on polymeric or inorganic matrices.

2.5 Heterogeneous base-catalysed transesterification

Based on the reaction mechanism described before for homogeneous catalysis, it is reasonable to assume that the basic sites on the catalytic support react with the methanol to give methoxide ion (CH_3O^-). The reaction mechanism proposed for a basic heterogeneous catalyst is show in figure 2.9 [8].

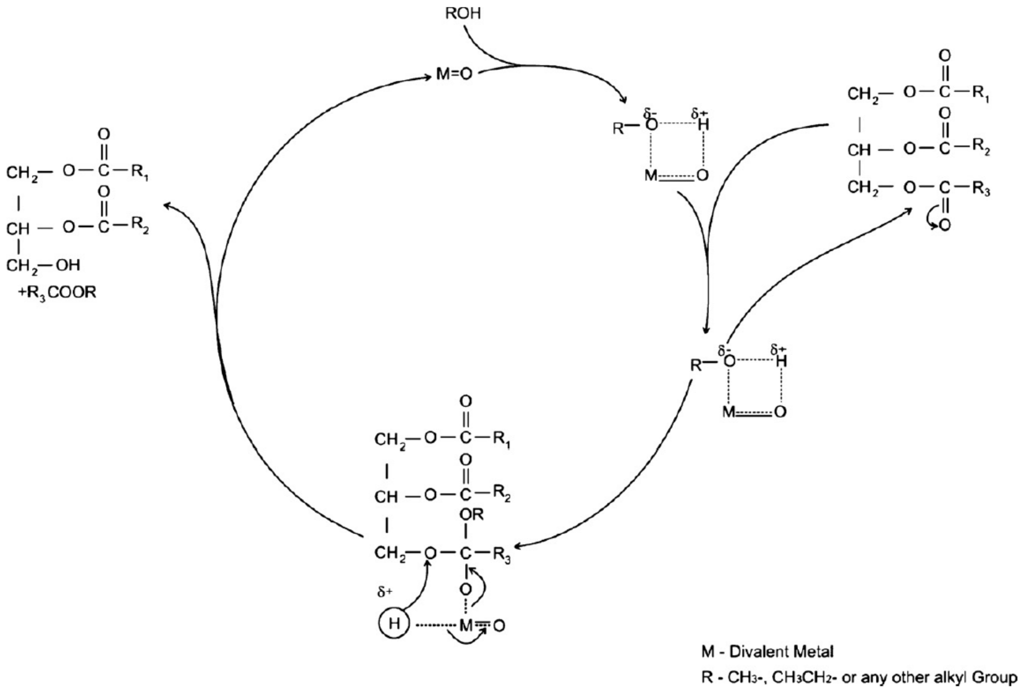


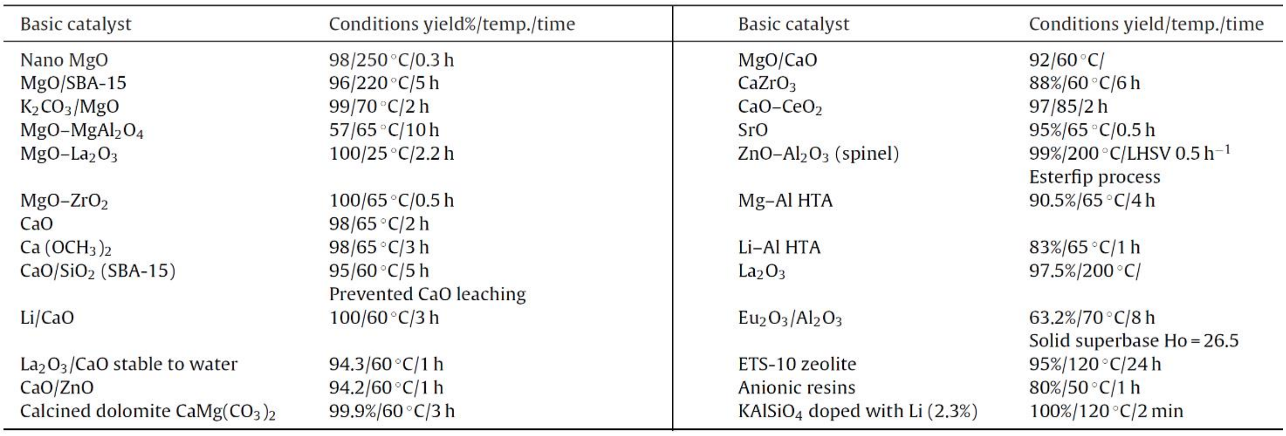
Figure 2.9. Mechanism of a general base heterogeneous catalyst for transesterification reaction [8].

CH_3O^- anion is the true catalytic species, di-glyceroxides and mono-glyceroxides anions have a poor solubility in oil phase and are affected by the attraction of the catalytic site in which they remain linked. The desorption stage of di-glyceroxides and mono-glyceroxides anions is very slow and for this reason, the basic heterogeneous catalysts are less active than homogeneous and require higher temperatures and higher alcohol to oil molar ratios [11].

The activity of the basic heterogeneous catalysts is, however, higher than that of the acidic heterogeneous catalysts. The major limitation to the application of heterogeneous basic catalysts is that they have the sensitivity towards the presence of water and FFAs in the reagent mixture. Similarly to homogeneous catalysts, heterogeneous basic ones cannot treat low-quality oils, but only refined oils. Heterogeneous basic catalysts are frequently subjected to leaching effect [13] and in many cases, it is difficult to discriminate between the catalytic contribution of the homogeneous and heterogeneous reaction [11]. Moreover, the reusability for the subsequent stages is a weak point for the application of these catalysts [8].

In general, a bivalent metal oxide, which has a high covalent nature, can catalyse the transesterification reaction. Alkaline earth metals such as Be, Mg, Ca, Sr, Ba and Ra, their oxides and derivatives are used in the literature. CaO, MgO and SrO catalyst are the most studied because the most effective for the transesterification reaction. The catalytic activity of these metal oxides is often dependent on the calcination temperature, since it determines the structure and the surface area [8].

A list of heterogeneous basic catalysts used in the literature is shown in figure 2.10 [11].



Basic catalyst	Conditions yield%/temp./time	Basic catalyst	Conditions yield/temp./time
Nano MgO	98/250 °C/0.3 h	MgO/CaO	92/60 °C/
MgO/SBA-15	96/220 °C/5 h	$CaZrO_3$	88%/60 °C/6 h
K_2CO_3/MgO	99/70 °C/2 h	CaO–CeO_2	97/85/2 h
MgO–$MgAl_2O_4$	57/65 °C/10 h	SrO	95%/65 °C/0.5 h
MgO–La_2O_3	100/25 °C/2.2 h	ZnO–Al_2O_3 (spinel)	99%/200 °C/LHSV 0.5 h^{-1} Esterfip process
MgO–ZrO_2	100/65 °C/0.5 h	Mg–Al HTA	90.5%/65 °C/4 h
CaO	98/65 °C/2 h		
Ca $(OCH_3)_2$	98/65 °C/3 h	Li–Al HTA	83%/65 °C/1 h
CaO/SiO_2 (SBA-15)	95/60 °C/5 h Prevented CaO leaching	La_2O_3	97.5%/200 °C/
Li/CaO	100/60 °C/3 h	Eu_2O_3/Al_2O_3	63.2%/70 °C/8 h Solid superbase Ho = 26.5
La_2O_3/CaO stable to water	94.3/60 °C/1 h	ETS-10 zeolite	95%/120 °C/24 h
CaO/ZnO	94.2/60 °C/1 h	Anionic resins	80%/50 °C/1 h
Calcined dolomite $CaMg(CO_3)_2$	99.9%/60 °C/3 h	$KAlSiO_4$ doped with Li (2.3%)	100%/120 °C/2 min

Figure 2.10. Heterogeneous basic catalysts, for the transesterification reaction, studied in the literature [11].

Hydrotalcites are very attractive catalysts, because, show high activities, are resistant to the presence of water and FFA [14] and give not place to leaching. The use of mixed oxides or an oxide support on another has the purpose to avoid the leaching due to the strong interaction between the two oxides and especially serves to introduce a bi feature that increases the resistance of the catalyst to water and free fatty acids [7].

The zeolite are employed as catalysts for heterogeneous catalysis. Zeolites are minerals structures containing silica and aluminium and certain cations such as Na^+, K^+, Ca^{2+}, Mg^{2+} in their structure, which give a basic nature. These catalysts are interesting because the pore size can be modulated and because resistant to high temperature. In addition, it is possible to dope the catalyst with other substances increasing the acidic or basic nature of the solid [8].

2.6 Enzymatic transesterification

Biodiesel can also be obtained with enzymatic catalysts, due to lipase enzyme's ability to catalyze the transesterification reaction. The operating temperature is very low, typically between 35 and 50 °C, but normally requires a much longer reaction time than the chemical catalysed systems. [17].

The benefits of bio catalysts for the production of biodiesel are the high selectivity, the low operating temperature and the ability to tolerate FFA and water. The disadvantages are related to the high cost of the enzymes, the high reaction time and the difficulties to reuse them. In fact, the enzyme is denatured very quickly, losing its activity [18]. Most lipases are also inhibited by high alcohol concentration [7].

The most studied enzymes are: Candida antartica [18], Candida rugasa, Pseudomonas cepacia [17], Pseudomonas spp. or Rhizomucar miehei [20]. The yield of biodiesel from this process can vary depending on the type of used enzyme [9].

To facilitate the recovery and increase the reuse it has been proposed to immobilize the enzyme on a solid support [19]. The catalyst was then placed inside a reactor fed with the mixture of reagents for the production of biodiesel in a continuous configuration.

In some cases, the activity and stability in terms of thermal, chemical and mechanical properties of the supported enzymes are, also, improved, thereby allowing their applications under harsher environmental conditions in term of pH, temperature and organic solvents [21].

2.7 Supercritical alcohol transesterification

Transesterification spontaneously occur at high temperatures also in the absence of catalysts [11]. In supercritical conditions, the dielectric constant of methanol varies giving it special properties. For this reason, in supercritical conditions methanol is able to solubilize the oil forming a single phase. The kinetics of the transesterification reaction increases because there is no resistance to the mass transport [6].

Transesterification with supercritical methanol is possible and the reaction requires less than 10 min at about 350 °C to reach almost quantitative conversion. Supercritical treatment at 350 °C, 43 MPa and 4 minute with a molar ratio methanol/oil equal to 42/1 was considered to be optimum for the transesterification of rapeseed oil into biodiesel fuel [7]. Moreover, esterification and transesterification occur together without problems and the reaction rate is not affected by the presence of water. It is then possible to use waste and/or not refined oils.

High-energy cost is a disadvantage of the supercritical process, a challenge in the development of supercritical process could be to reduce further the reaction time, by operating in the presence of an opportune catalyst, at lower temperature and pressure, for rendering more attractive this technology [22].

2.8 Ultrasound and Microwave assisted transesterification

Ultrasound is a high frequency sound (2–10 MHz). The energy of ultrasonic irradiation can activate various mechanisms, so it can have physical and chemical effect on heterogeneous reaction systems through cavitation of bubbles [23]. When ultrasound passes through the liquid, it consists of both expansion and compression waves. The collapse of the cavitation bubbles generates micro-turbulence, increase the mass and heat transfer in the liquid, and cause velocity gradients that result in shear stresses [24]. Most researchers believe that physical effect of ultrasound on the formation of the fine emulsion between immiscible fluids is responsible for accelerating the transesterification reaction [1].

Microwave irradiation is another alternative efficient heating method used to shorten the transesterification. The microwave irradiation potentially can be an efficient and cost-competitive technique for large-scale biodiesel production. Its advantages are a drastic reduction in the quantity of by-products and a short separation time [25].

Some authors have shown that the application of ultrasound and microwaves are able to improve the process. The techniques can also be used together to obtain more benefits [26].

2.9 Experimental section

2.9.1 Materials

Refined rapeseed oil used in this study was purchased from a local supermarket. Its fatty acid composition was determined as reported after and it is summarized in Table 2.1. Methanol (HPLC grade >99,8%) from Carlo Erba Reagents was used as alcohol. Tin (II) oxide (99.9%) was purchased from Alfa Aesar and used as heterogeneous catalyst for the transesterification experiments. The native catalyst powder was ground with a laboratory mortar under inert environment in a glove box.

Sodium methoxide (98%) was purchased from Alfa Aesar and used as homogeneous catalyst for the quantitative transesterification performed to characterize the rapeseed oil. Citric acid (99%) Sigma-Aldrich was used to neutralize the basic mixture obtained at the end of the transesterification reaction.

Methyl palmitate (C 16:0, ≥99%), methyl stearate (C 18:0, ~99%), methyl oleate (C 18:1, 99%), methyl linoleate (C 18:2, ≥99%), methyl linolenate (C 18:3, ≥99%), and glycerol (99%) were purchased from Sigma-Aldrich and used for GC calibration. Tetrahydrofuran (THF) (Chromasolv >99%) from Aldrich, methyl heptadecanoate (analytical standard 99%) from Fluka, were used, as diluent and internal standards respectively for the GC analysis of the product.

2.9.2 Reaction system and procedures

All experiments were conducted in a batch reactor in AISI 316 with a free volume of 20 mL specially designed. A magnetic stir bar provides agitation of the mixture. A type K thermocouple and a pressure transducer were used to measure the values of temperature and pressure, respectively. A valve connected to the system was used to purge the loaded reactor with argon. The reactor temperature was kept constant by a metal block heated by electrical resistances controlled by a PID controller.

In a typical transesterification experiment, a certain amount of rapeseed oil and methanol were weighed on a Sartorius CP 225D balance using capped vial to prevent loss of alcohol by evaporation. The catalyst, was weighed and quickly loaded into the reactor together with the reactant, then the reactor was sealed.

The free volume of the reactor was washed with low pressure argon for six times to eliminate oxygen. The reactor was then inserted into the metal block and heated to selected reaction temperature while stirring was initiated. Most of the experiments were carried out at 473 K, since the average heating rate of the heating system was 13 K/min, the reactor reached the operating temperature in about 14 minutes.

Studying the effect of temperature on the performances of the catalyst we have found that below 443 K reaction rate is negligible, the real transient time is about 5 minutes. For this reason, the total heating period was not considered and the measurement of the reaction time started when the temperature reached the set point value. At the end of the reaction, the reactor was removed from the heating system and was rapidly cooled to room temperature by immersion in a bath of water and ice. Then it was dried and opened to recover the products and the catalyst. The liquid solution and the catalyst were carefully transferred into a glass vial. The sample was centrifuged at 3000 rpm for 20 minutes, to separate the catalyst. The liquid mixture was collected and moved to a clean vial.

2.9.3 Analytical techniques

The concentrations of alkyl esters and glycerol in the samples were measured using a Agilent 7890B Gas Chromatograph (GC) equipped with a RESTEK Superchrom FAMEWAX capillary column (length 30 m, external diameter 0.32 mm, internal diameter 0.25 mm) using a Flame Ionization Detector (FID) and helium 5.0 as carrier gas. The GC oven temperature was set at 438 K for 22 min, then it was increased with a heating rate of 5 K/min up to 493 K and maintained for 5 min. Calibration was accomplished for fatty acid methyl esters (FAMEs) and glycerol by preparing solutions of known concentration of pure alkyl esters (C 16:0, C 18:0, C 18:1, C 18:2, C 18:3) and glycerol, using methyl heptadecanoate as internal standards. This component is never present in the mixture to be analysed and has a well-defined peak and a retention time similar to that of other species but clearly distinct from them. The internal standard method allows to obtain very accurate results and is not particularly sensitive to variations of the amount of sample injected into the column. The concentration of each ester produced by the reaction is related to the internal standard introduced in sample preparation according to the following linear relationship:

$$\frac{M_i}{M_s} = f * \frac{A_i}{A_s}$$

where M_i and A_i are the mass and the i-th component signal area, M_s and A_s are the concentration and area related to the internal standard, and f_i the response factor of the generic ester.

For the compounds C 20:1 and C 22:1 whose standard were not available the same response factor of the compound C 18:3 was assumed to perform quantization. Cumulative yields in fatty acid methyl esters Y_{FAME} was computed according to the following formula:

$$Y_{FAME} = \frac{M_{FAME}}{W_{Oil}^0}$$

where M_{FAME} is the mass of free fatty acid methyl esters determined from the GC calibration and W^0_{oil} is the initial mass of rapeseed oil loaded in the reactor. The same calculation procedure was used to quantify the glycerol present in the reaction mixture, but the column was unable to measure it correctly. For this reason, the data relating to glycerol are not reported in the results.

As said earlier, the reagent system consists of two immiscible phases: the alcohol phase and the oil phase. At the end also the products are separated into two phases, in particular the esters will form a FAME rich phase together with the unreacted triglycerides, while the glycerol and the non-reacted alcohol will form the alcohol phase. The existence of a two-phase system has created problems for the analysis of the sample, since it is necessary to know the mass of the two phases and a possible physical separation would lead to a too high error. This problem was overcome by adding a known amount of tetrahydrofuran (THF) which has the ability to solubilize both phases thus obtaining a homogeneous solution.

2.9.4 Determination of the composition of rapeseed oil

To determine the typical fatty acid composition of the adopted vegetable oil, it was quantitatively converted into FAMEs by transesterification with methanol. Sodium methoxide (CH_3ONa) was used as it is the most active homogeneous catalyst for this reaction.

Loading procedure, reaction and product separation were performed according to procedure reported in the literature [27]. The reaction was carried out dissolving 200.2 mg of sodium methoxide in 20.03 g of methanol. This solution was mixed with 10.003 g of the rapeseed oil. The alcohol is in strong stoichiometric excess compared to the oil to obtain quantitative conversion of all triglycerides. The reaction was performed at the normal boiling point of methanol in a glass flask heated by an electric mantle with a temperature controller. The flask was equipped with a condenser cooled by water at room temperature to trap the evaporated alcohol. The reaction mixture was vigorously stirred by a magnetic stir bar during the experiment.

Reaction lasted 4 hours then the system was cooled to room temperature and two distinct phases were obtained. A heavy glycerol-rich phase deposited at the bottom and a supernatant FAME-rich phase.

The latter was recovered and washed four times at 50 °C with an aqueous solution of citric acid 5% w/w to neutralize the catalyst and other four more times with distilled water. Finally, the FAME-rich solution was evaporated in a rotavapor at 80 ° C for 1 hour to remove methanol [27].

The FAME distribution of the vegetable oil was determined by GC analysis of this mixture. Rapeseed oil composition found and used in this study is summarized in Table 2.1.

Fatty acid **(C-length : no.=bonds)**	16:0	18:1	18:2	18:3	20:1	22:1
% w/w	4.5	66.3	16.5	10.8	1.7	0.3

Table 2.1. Fatty acid composition of the vegetable oil used in this study.

2.10 Results and Discussion

The majority of the experiments was carried out in the reactor by loading 4.0 g of rapeseed oil, 3.2 g of methanol, 200 mg of catalyst. The first tests were carried out using zirconium tungstate ($Zr(WO_4)_2$), niobium phosphate ($NbPO_4$), and tin (II) oxide (SnO). These catalysts are chosen because they have acid behaviour therefore can influence the transesterification reaction.

Catalyst	**Temperature [K]**	**Time [h]**	**Mass ratio catalyst /oil [g/g]**	**Molar ratio methanol/oil [mol/mol]**	**FAME Yield [% w/w]**	**Note**
-	473	1	0.00	22	7.3	Catalyst free test
SnO	473	1	0.05	22	77.9	
SnO	483	1	0.05	22	84.3	
$Zr(WO_4)_2$	483	1	0.05	22	12.2	
$NbPO_4$	483	1	0.05	22	7.7	

Table 2.2. Comparison of the catalysts tested under the same operating conditions.

A comparison between the performance of different catalysts on the transesterification reaction is summarized in Table 2.2. The results of a test without catalyst is also shown for highlighting the effect of catalysis: we found a yield of esters of only 7.3 %. The yield of methyl esters obtained with $Zr(WO_4)_2$ and $NbPO_4$ catalysts were 12.2% and 7.7% respectively, so we can conclude that these catalysts have a low activity for the studied reaction. Otherwise, the SnO catalyst led to a FAME yield of 84.3% and it proved to be a good catalyst for the transesterification reaction. In addition, the catalyst allows reaching very high yields of biodiesel even in very mild operating conditions when compared to supercritical process.

Other experiments with the SnO catalyst were carried out by varying the operating conditions and the parameters that most affect the transesterification reaction.

2.10.1 Effect of the reaction temperature and of the methanol to oil molar ratio

The transesterification of rapeseed oil with methanol was studied as a function of the reaction temperature using a fixed molar ratio of methanol to oil of 22 and a ratio of catalyst to oil 0.33 mol/mol. Experiments performed at 423 K and 443 K gave very low yields of methyl esters (Figure 2.11). Increasing the reaction temperature to 463 K yields of methyl esters was 20.7%. These results indicate that the tin oxide catalyst needs a minimum temperature to be active in the transesterification reaction. When the temperature was increased to 473 and 483 K FAME yields increased to 77.9 % and 84.3% respectively.

A further increase in the reaction temperature to 493 K had no positive effect on the yield, which remained almost constant up to 503 K. At a temperature of 513 K the yield of esters was 78.7%. This decrease could be attributed to a limited thermal stability of the double bonds present in the acid fatty at this temperature.

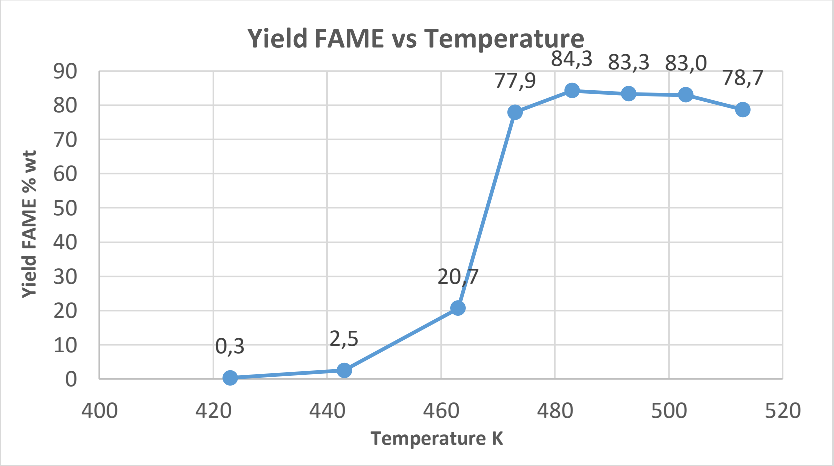


Figure 2.11. Transesterification of rapeseed oil with tin oxide using methanol: effect of the reaction temperature. Molar ratio methanol to oil = 22 and catalyst to oil = 0.33; reaction time 1 hour.

A set of transesterification experiments in the presence of SnO at molar ratio of catalyst to oil of 0.33 was carried out changing the molar ratio of methanol to vegetable oil from 5.5 to 44 at 473 K with reaction times of 4 hours. When the methanol/oil ratio was increased from 5.5 to 11 the yield of methyl esters increased from 45.2% to 76.0%. A further increase of the molar ratio between methanol and oil to 22 and 44 led to an increase in the ester yield to 83.8% and 92.5% respectively.

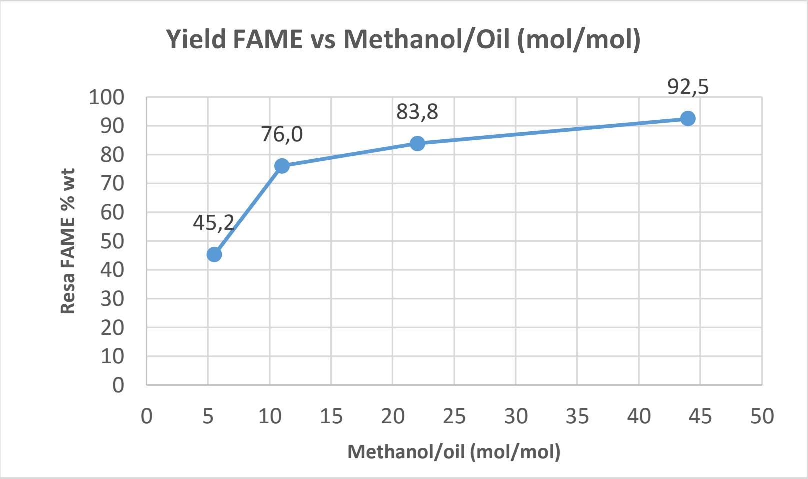


Figure 2.12. Transesterification of rapeseed oil with tin oxide using methanol: effect of the methanol to oil molar ratio. Temperature 473 K, molar ratio catalyst to oil = 0.33, reaction time 4 hour.

It is generally accepted that the transesterification reaction involves three consecutive steps that are characterized by reversibility. When the molar ratio between methanol and oil increases each step is shifted to the products and the yields in FAME increases. The obtained results are shown in Figure 2.12 and confirm that the increase of the concentration of the methanol improves the yields in esters.

2.10.2 Effect of the catalyst concentration and reaction time

The effect of the tin oxide *concentration* has been studied for the reaction of transesterification of rapeseed oil. The tests were all carried out at the temperature of 473 K, one hour of treatment and with a molar ratio of methanol to oil of 22 (Figure 2.13). FAME yield of 65.6% was found when the oil catalyst ratio was 0.1. Doubling and quadrupling the concentration of catalyst the yield was 77.9 and 82.8% respectively. The higher the concentration of catalyst the higher the FAME yields at fixed reaction time that is a clear indication of faster global rate of reaction. However, at high conversion it is possible to observe a gradual decrease of the reaction rate with the catalyst loading: this behaviour could be attributed to the onset of mass transfer control on the rate of the reaction when high enough triglyceride conversion are reached.

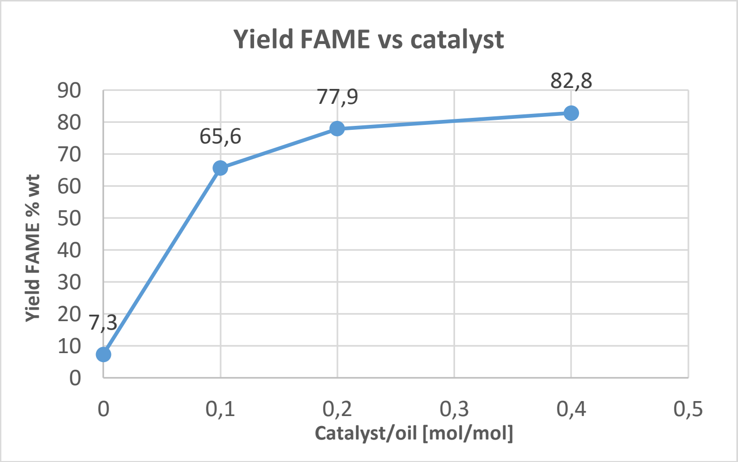


Figure 2.13. Transesterification of rapeseed oil with tin oxide: effect of the catalyst concentration. Temperature 473 K, initial molar ratio of methanol to oil = 22, reaction time 1 hour.

Another important parameter for the transesterification reaction is the treatment time. Transesterification experiments of rapeseed oil with methanol were conducted using a molar ratio of methanol to oil of 22, temperature of 473 K and molar concentration of SnO catalyst to oil of 0.33, by varying the time of treatment from 0.25 to 4 hours. The results obtained are shown in Figure 2.14.

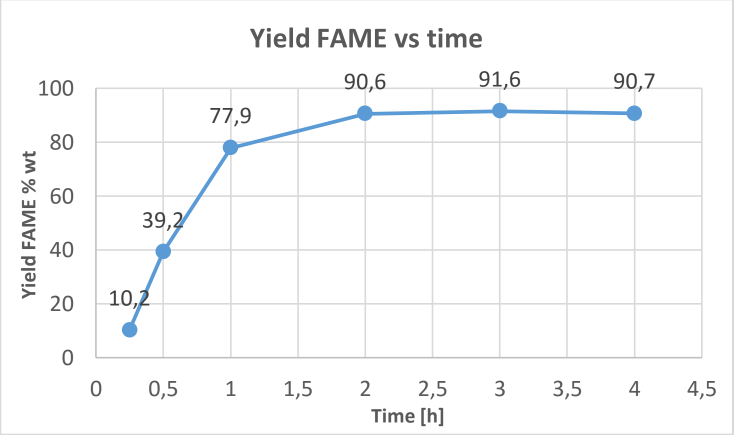


Figure 2.14. Transesterification of rapeseed oil with tin oxide: effect of the reaction time. Temperature 473 K, initial molar ratio of methanol to oil = 22, molar concentration of SnO catalyst to oil = 0.33.

When the treatment time was increased from 0.25 to 0.5 the yield changed from 10.2 to 39.2% respectively, while for one and two hours of treatment, the yield was 77.9 and 90.6%. Increasing the treatment time at three and four hours, the yield remained virtually constant. This result suggests that in these operating conditions after two hours of treatment, the reaction is close to the thermodynamic equilibrium.

2.10 Conclusions

Several acidic heterogeneous catalysts were studied for the transesterification reaction of rapeseed oil with methanol. The catalyst tin (II) oxide was found most active among those tested. The most important parameters of the process such as temperature, molar ratio of reactants, catalyst concentration and treatment time were studied in the presence of the tin (II) oxide catalyst. The temperature of 473 K and the molar ratio methanol to oil of 22 were found acceptable operating conditions to achieve high conversions of oil. Further increasing these values, the increase in the yield of esters is weak, while from the industrial point of view the cost of the process would increase. The same considerations can be made for the other operating parameters: use of high catalyst concentrations and high treatment times was beneficial for the conversion of triglycerides, but the operating costs for an industrial application would increase. At the basis of the results obtained, a catalyst to oil molar ratio of 0.1, and treatment time 1 hour, can be considered sufficient to achieve significant yields of biodiesel.

In conclusion, the catalyst tin (II) oxide was shown to be an effective catalyst for the transesterification reaction as high yields of the methyl esters were reached in relatively mild operating conditions when compared to supercritical process.

REFERENCE

[1] V. B. Veljkovic´, J. M. Avramovic´, O. S. Stamenkovic´. Biodiesel production by ultrasound-assisted transesterification: State of the art and the perspectives 2012, 16(2), 1193–1209.

[2] U. Schuchardt, R. Sercheli, R.M.Vargas. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc., 1998, 9(1), 199-210.

[3] Freedman B., Pryde E.H., Mounts T.L. Variables affecting the yields of fatty esters from transesterified vegetable oils. J. Am. Oil Chem. Soc. 1984;61:1638.

[4] M. Canakci, J. Van Gerpen, Biodiesel production via acid catalysis, American Society of Agricultural Engineers, 1999, 42(5): 1203-1210.

[5] E. Lotero, Y. Liu, D. E. Lopez, K. Suwannakarn, D. A. Bruce, J. G. Goodwin, Jr. Synthesis of Biodiesel via Acid Catalysis, Ind. Eng. Chem. Res. 2005, 44, 5353-5363.

[6] Leung DYC, Wu X, Leung MKH. A review on biodiesel production using catalysed transesterification. Appl Energy 2010;87:1083–95.

[7] Z. Helwani, M.R. Othman, N. Aziz, J. Kim, W.J.N. Fernando. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review. Applied Catalysis A: General 363 (2009) 1–10.

[8] A.P. Singh Chouhan, A.K. Sarma. Modern heterogeneous catalysts for biodiesel production: A comprehensive review. Renewable and Sustainable Energy Reviews 15 (2011) 4378– 4399.

[9] A. F. Lee, J. A. Bennett, J. C. Manayil, K. Wilson. Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification. Chem. Soc. Rev., 2014,43, 7887-7916.

[10] De Almeida Rusiene M, Noda Lucia K, Goncalves Norberto S, Meneghetti Simoni MP, Meneghetti Mario R. Transesterification reaction of vegetable oils, using superacid sulfated TiO2–base catalysts. Appl Catal A: Gen 2008;347: 100–5.

[11] E. Santacesaria, G. M. Vicente, M. Di Serio, R. Tessera. Main technologies in biodiesel production: State of the art and future challenges. Catalysis Today 195 (2012) 2– 13.

[12] Alsalme A, Kozhevnikova EF, Kozhevnikov IV. Heteropoly acids as catalysts for liquid-phase esterification and transesterification. Appl Catal A: Gen 2008;349:170–6.

[13] M. Di Serio, R. Tesser, L. Casale, A. D'Angelo, M. Trifuoggi, E. Santacesaria, Heterogeneous catalysis in biodiesel production: the influence of leaching, Topics in Catalysis 53 (2010) 811–819.

[14] M. Di Serio, M. Ledda, M. Cozzolino, G. Minutillo, R. Tesser, E. Santacesaria, Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts, Industrial and Engineering Chemistry Research 45 (2006) 3009–3014.

[15] O.S. Stamenkovi, M.L. Lazic, V.B. Veljkovic, D.U. Skala, Biodiesel production by enzyme-catalyzed transesterification, Hemijska Ind. 59 (2005) 49–59.

[16] J. Van Gerpen, B. Shanks, R. Pruszko, D. Clements, G. Knothe, August 2002– January 2004, National Renewable Energy Laboratory (NREL), Colorado, July 2004 [NREL/SR-510-36240].

[17] S. Shah, M.N. Gupta, Lipase catalyzed preparation of biodiesel from Jatropha oil in a solvent free system. Process Biochem. 42 (2007) 409–414.

[18] D. Royon, M. Daz, G. Ellenrieder, S. Locatelli, Enzymatic production of biodiesel from cotton seed oil using t-butanol as a solvent. Bioresour. Technol. 98 (2007) 648– 653.

[19] O.L. Bernardes, J.V. Bevilaqua, M.C.M.R. Leal, D.M.G. Freire, M.A.P. Langone, Biodiesel fuel production by the transesterification reaction of soybean oil using immobilized lipase. Appl. Biochem. Biotechnol. 137–140 (2007) 105–114.

[20] O.M. Lai, H.M. Ghazali, C.L. Chong, Use of enzymatic transesterified palm stearin-sunflower oil blends in the preparation of table margarine formulation, Food Chem. 64 (1999) 83–88.

[21] Casas, A; Ramos, MJ; Perez, A. Production of Biodiesel through Interesterification of Triglycerides with Methyl Acetate, ISBN: 978-1-62808-565-5. Editor: David A. Sanders. © 2013 Nova Science Publishers, Inc.

[22] S.J. Yoo, H.-S. Lee, B. Veriansyah, J. Kim, J.-D. Kim, Y.-W. Lee, Synthesis of biodiesel from rapeseed oil using supercritical methanol with metal oxide catalysts, Bioresource Technology 101 (2010) 8686–8689.

[23] Mason TJ, Lorimer JP. Applied sonochemistry: uses of power ultrasound in chemistry and processing. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co.; 2002.

[24] Adewuyi YG. Sonochemistry: environmental science and engineering applications. Ind Eng Chem Res 2001;40:4681–715.

[25] Hernando J, Leton P, Matia MP, Novella JL, Alvarez-Builla J. Biodiesel and FAME synthesis assisted by microwaves: homogeneous batch and flow processes. Fuel 2007;86:1641–4.

[26] Hsiao M-C, Lin C-C, Chang Y-H, Chen L-C. Ultrasonic mixing and closed microwave irradiation-assisted transesterification of soybean oil. Fuel 2010;89:3618–22.

[27] KoohiKamali S., Tan CP, Ling TC. Optimization of Sunflower Oil Transesterification Process Using Sodium Methoxide. The Scientific World Journal, vol. 2012, Article ID 475027, 8 pages, 2012.

Chapter 3

BIODIESEL PRODUCTIN USING INTERESTERIFICATION REACTIONS

3.1 Introduction

As explained in the previous chapter, during the transesterification, triglycerides (TGs) react with methanol producing fatty acid methyl esters (FAME) and glycerol. To carry out this reaction in mild conditions the utilization of catalysts is necessary. Acidic or basic catalysts are needed to obtain high reaction rate at low operating temperatures. The main problem of the biodiesel production through transesterification reaction is its low profitability [1]. This situation is due to the high price of raw vegetable oil. In addition, the glycerol obtained as a co-product is difficult to sell due to its limited market and is normally managed as a waste product [2].

However by interesterification, glycerol can be converted into a higher added-value product such as glycerol triacetate (triacetin). In fact the replacement of alcohol with methyl acetate (or ethyl acetate) produces methyl esters (or ethyl esters) and triacetin (TA) as a co-product instead of glycerol. This route is called interesterification reaction. The main applications of the triacetin are as a plasticizer and gelatinizing agent in polymers and explosives [3]. Moreover, it has been considered that triacetin can be used as a biodiesel additive [4,5].

Interesterification consists of three consecutive reversible reactions, as shown in Figure 3.1. The triglycerides are converted into monoacetindiglycerides, diacetinmonoglycerides and triacetin, releasing a molecule of fatty acid methyl ester in each step [1].

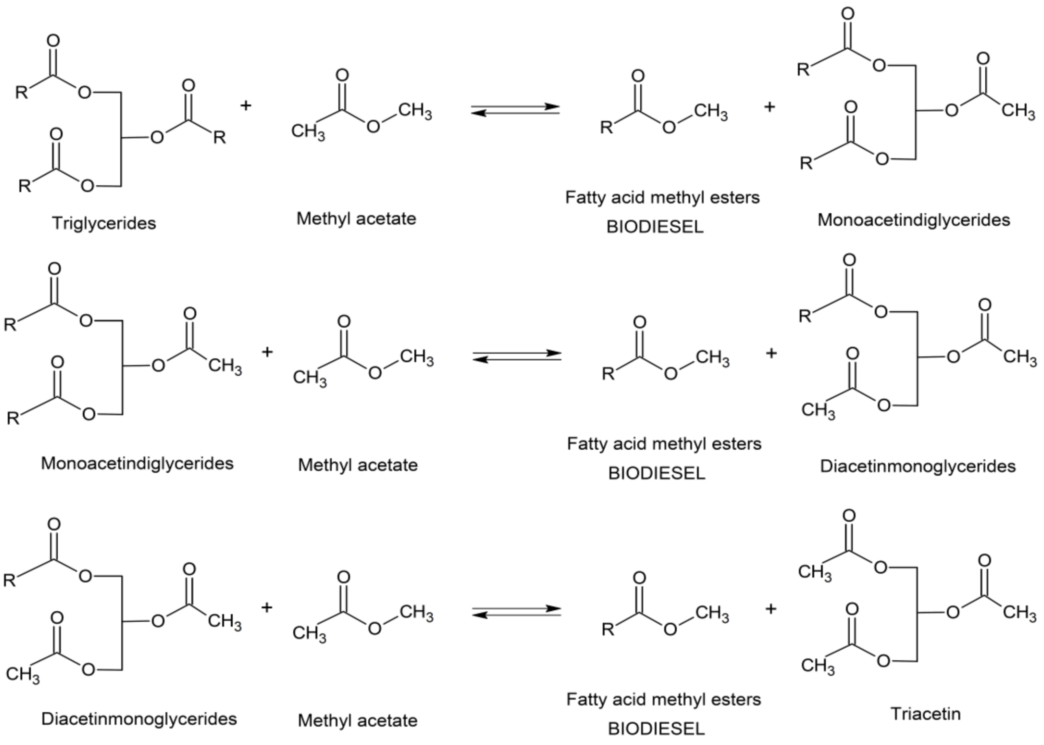


Figure 3.1. Consecutive interesterification of triglycerides with methyl acetate [1].

In contrast to the transesterification, during the interesterification, one ester exchanges its alcohol with another ester group. The reactants and products are miscible, therefore there are no resistance to mass transport [1].

The interesterification of triglycerides with methyl acetate can be carried out using chemical catalysts, supercritical methyl acetate and enzyme.

3.2 Influence of triacetin on biodiesel quality

Some literature studies showed that a certain amount of triacetin, if present in the mixture of FAME, can be considered as a component of biodiesel formulation. The European standard EN 14214 and American ASTM D6751 are quality standards for fuel sold in Europe and America. The regulations contain a number of parameters and the limiting values that the fuel must meet to be marketable. The most important parameters are: density, kinematic viscosity, low temperature parameters (i.e., cloud point and cold filter plugging point), cetane number, methyl ester content, distillation temperature, flash point and oxidation stability. Triacetin partially modifies the chemical and physical properties of the biofuel, but if its concentration does not cross fixed limits the fuel complies with current regulations and can be sold to power diesel engines. The **density** of the fuel is important for the operation of the diesel engine because during operation very precise volumes of fuel are injected in cylinders. Triacetin has a density of 1183 kg/m^3 the esters of the fatty acids have a density range between 860-900 kg/m^3, while the density of the fossil diesel is 800-850 kg / m^3. The presence of triacetin increases the density of the mixture and this could be a problem for the European legislation that imposes the upper and lower values between 860 and 900 kg/m^3.

The addition of triacetin cause a linear increase of the density. The upper limit depends on the density of the esters present in the mixture. For low-density oils such as palm oil, 13.5 % w/w is the maximum allowed limit of TA, while for very dense oils such as soybean oil the maximum limit decreases to 9.5% w/w.

The American legislation instead does not place limits on the fuel density and therefore the concentration of triacetin can reach the maximum obtainable from the stoichiometry of the reaction of interesterification (20% w/w).

The **kinematic viscosity** of biodiesel is important because it influences the engine injection system, the atomization of the fuel and thereby the combustion temperature.

Triacetin has a kinematic viscosity almost double compared to that of esters of fatty acids and to that of the diesel fuel. The high concentration of triacetin in the blend of biodiesel does not cause drastic changes in kinematic viscosity. Therefore, the content of the triacetin may be present up to the maximum obtainable from the reaction.

A disadvantage in the use of biodiesel, compared to fossil diesel, is the behaviour at low temperatures. The high content of saturated esters with high solidification points causes the formation of solid precipitates at temperatures higher than those of the gas oil. The most important parameters that are used to describe the cold behaviour of biodiesel are the **cloud point (CP)**, the **pour point (PP)** and the **cold filter plugging point (CFPP)**. The cloud point is the temperature at which a liquid mixture becomes cloudy due to the crystallization of the species with higher solidification temperature. The pour point is the lowest temperature at which a fluid is able to flow under the influence of gravity. Finally, the cold filter plugging point represents the highest temperature at which a liquid is no longer able to pass through a standard filtering device in a given time interval and cooling under standardized conditions. The presence of triacetin according to some studies, does not adversely affect the parameters CP, PP CFPP and therefore do not impose maximum limits regulations.

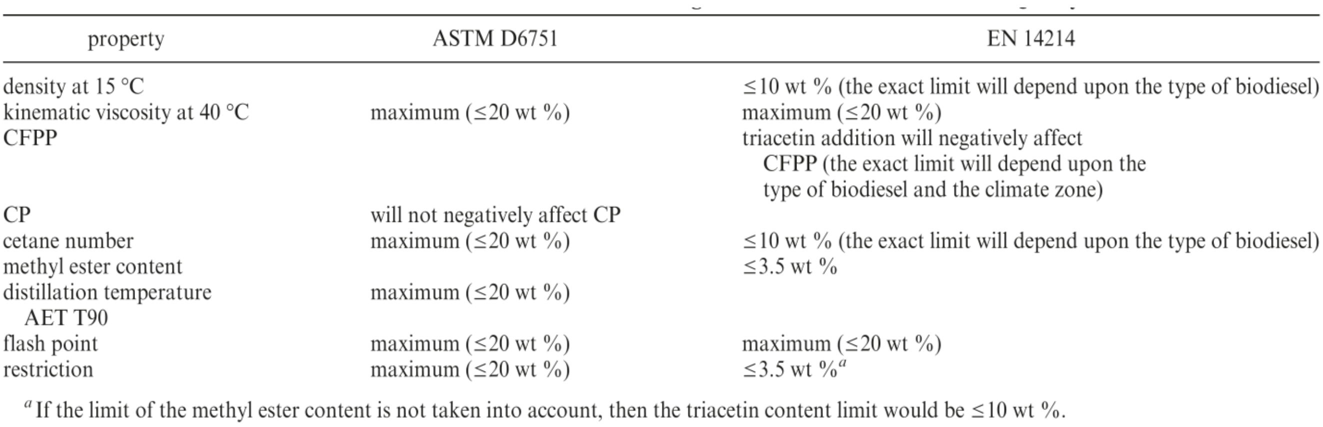
The **cetane number** is a measure of the quality of combustion of diesel fuel. The cetane number is found by carrying out tests on an engine under standard conditions using a mixture of hexadecane and isocetane as reference. The pure triacetin has a number of very low cetane rating compared to esters, therefore, the presence of triacetin in the mixture decreases the cetane number of the biodiesel. The European legislation requires to use a value not higher than 10% by weight, while the American is less restrictive.

The **higher heating value** (HHV) is the amount of heat released from the burning of the unit mass of a substance. From this parameter, it depends on the fuel consumption of an engine. Biodiesel has a HHV of slightly less than that of fossil diesel because of the presence of oxygen atoms present in the ester group. The oxygen content in triacetin (49.5 % w/w) is greater than that of biodiesel (11% w/w), therefore the calorific value of triacetin is less than that of biodiesel. The increased concentration of triacetin decreases slightly the higher heating value of mixture. However, there are no minimum values HHV be respected both in the American and European legislation, and triacetin may be present in high concentrations.

The biodiesel **distillation temperature** is used to assess its purity according with the foreign content. Usually, it defines T90 i.e. the temperature at which 90% by volume of the initial mixture is recovered. This parameter serves to highlight the possible presence of heavier impurities of esters. Triacetin is relatively vaporisable, therefore, it does not increase the T90. The American legislation sets the upper limit for the T90 of a biodiesel at 360 °C, while the EU does not set any limits.

The **flash point** of the mixture serves to detect the possible presence of compounds more volatile than esters. Biodiesel has a higher flash point compared to fossil diesel and triacetin has an even lower boiling temperature. Consequently the presence of triacetin in biodiesel leads to a decrease of the flash-point value. The reduction in the flash point is not drastic, and the value is always maintained in the range dictated by the guidelines.

Based on what discussed above, it is possible to make a table of contents for the maximum quantity of triacetin that you can add to the biodiesel mixture. The figure 3.2 shows the limits imposed by the American and European guidelines.



property	ASTM D6751	EN 14214
density at 15 °C		≤10 wt % (the exact limit will depend upon the type of biodiesel)
kinematic viscosity at 40 °C	maximum (≤20 wt %)	maximum (≤20 wt %)
CFPP		triacetin addition will negatively affect CFPP (the exact limit will depend upon the type of biodiesel and the climate zone)
CP	will not negatively affect CP	
cetane number	maximum (≤20 wt %)	≤10 wt % (the exact limit will depend upon the type of biodiesel)
methyl ester content		≤3.5 wt %
distillation temperature AET T90	maximum (≤20 wt %)	
flash point	maximum (≤20 wt %)	maximum (≤20 wt %)
restriction	maximum (≤20 wt %)	≤3.5 wt %^{a}

^{a} If the limit of the methyl ester content is not taken into account, then the triacetin content limit would be ≤10 wt %.

Figure 3.2. Triacetin limit values present in biodiesel according to European and American standards [17].

It must be noticed that for the European legislation limits are more stringent, in particular because of the concentration of esters the maximum amount of triacetin is fixed at 3.5% w/w. The American legislation does not limit the content of triacetin that may 20% w/w.

3.3 Chemical Interesterification

3.3.1 Basic catalyst

Base and acid catalysts have been used in the chemical interesterification of triglycerides with methyl acetate.

Casas et al. have studied the process of interesterification of triglycerides with methyl acetate using a catalyst such as hydroxide, methoxide and polyethylenglycols (PEG), potassium [19].

The figure 3.3 shows the variation of the weight fraction of esters in the reaction mixture with the reaction time. The reaction conditions are very mild: 50 °C temperature, molar ratio methyl acetate / oil = 12, molar ratio catalyst / oil = 0.2. Assuming a 100% conversion of the TG esters constitute the 80.2% w/w of the mixture of products, while the remaining 19.8% consists of the triacetin.

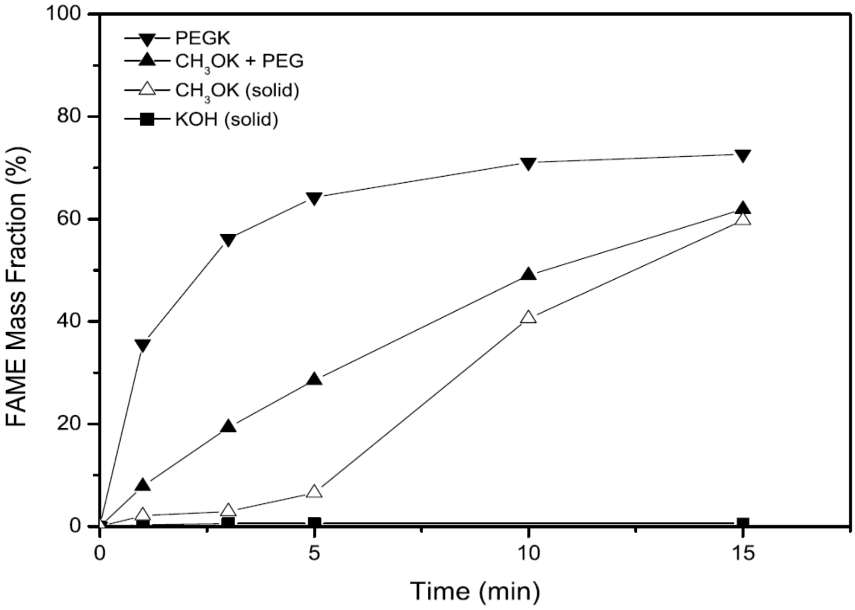


Figure 3.3. Chemical interesterification of oil in methyl acetate. Trend in the proportion by weight of esters, vs. time, for various basic catalysts at 50°C temperature, molar ratio methyl acetate / oil = 12, molar ratio catalyst / oil = 0.2 [19].

The potassium hydroxide exhibited no activity in catalysing the reaction of interesterification. In the transesterification process, the hydroxide reacts with alcohol to form the alkoxide, which is the true active species that catalyzes the reaction. In this case, the methyl acetate is present in place of alcohol and the alkoxide cannot be formed. In addition, the hydroxide tends to react irreversibly forming potassium acetate, which is an undesirable compound. Unlike, the potassium methoxide is able to effectively catalyze the reaction, providing significant yields already after 15 min of reaction. However, there is a 5 min induction range where the kinetics of the reaction is much slower. This is due to the poor solubility of potassium methoxide in methyl acetate in the oil and, therefore, the transport of material from the solid catalyst to the liquid phase strongly limits the kinetics of the process. The addition of PEG to potassium methoxide eliminates the induction period and increases the kinetics in the first minutes of the reaction. The potassium methoxide is able to form complexes (PEGK) with PEG, which increases the solubility in the phase rich in esters. The formation of these complexes can take place simultaneously with the reaction of interesterification. Otherwise, if the complex PEGK are previously formed and then added to the reactants, then the kinetics of reaction increases and reaches a high yield in 15 min. However, the use of the PEG requires an extraction with water for its removal from the reaction products and this adds a step to the production process.

An alternative to the utilization of PEG may be to premix the catalyst with one of the two reactants (see Figure 3.4). As shown in the figure, the pre-mixing of catalyst and oil has considerably increased the kinetics since the early minutes of reaction and the yields obtained are comparable to those obtained with PEGK.

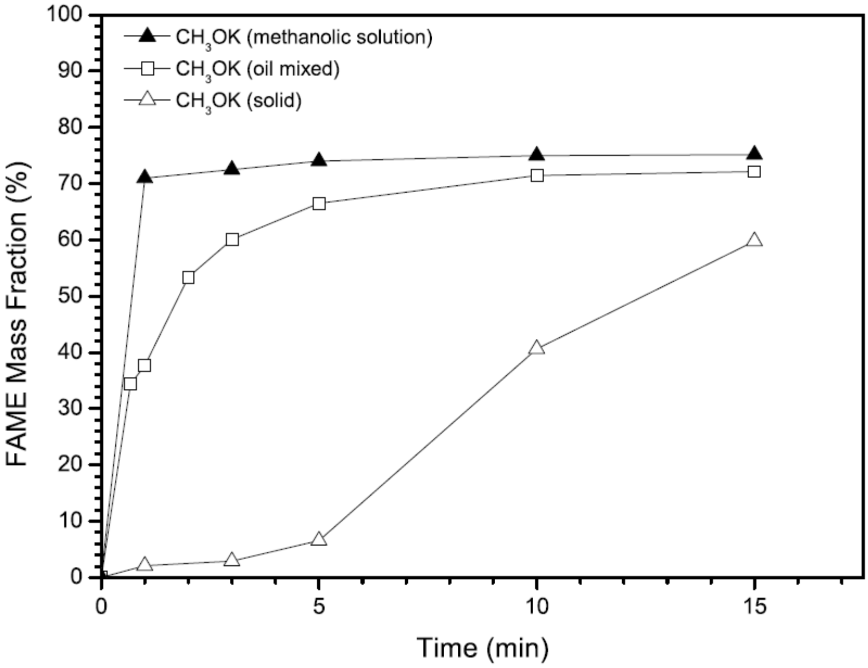


Figure 3.4. Chemical interesterification. Trend in the proportion by weight of esters to vary the time for pre-mixed systems. Temperature 50 °C, molar ratio methyl acetate / oil = 12, molar ratio catalyst / oil = 0.2 [19].

This result confirms the fact that the transport of catalyst unit from the solid phase to the liquid phase is a crucial step of the process [6].

The pre-mixing of the catalyst with methyl acetate leads to a decrease of the maximum attainable yield despite the fact that, even in this case, there is an increase of the kinetics in the first minutes of the reaction. This is probably due to the presence of secondary reactions between the catalyst and methyl acetate with consequent formation of unwanted species that block the reaction of interesterification.

As well as for the transesterification, also in the reaction of interesterification the presence of water leads to a deactivation of the catalyst and to a reduction in the yield of esters and triacetin. The water in concentration greater than 100 ppm can significantly inhibit the reaction. Therefore, the use of non-dried reagents forces the use of high catalyst concentrations [19].

The interesterification of rapeseed oil using tin (II) octanoate as homogeneous catalyst has been recently studied. This catalyst was found to be completely soluble in the reaction system at investigated concentrations and allowed the operator to reach FAME yields close to 90% and TA yield of about 60% after 20 hours of batch reaction at 210 °C with initial methyl acetate to oil molar ratio of 40 [7].

In recent years, many research groups have tried to develop heterogeneous catalysts immobilizing catalytic species especially of organic nature, on polymeric solid supports, or encapsulated in zeolite supports [8].

Xie W. and co-workers have prepared and studied a catalyst with KNO_3 supported on alumina, for the reaction of chemical interesterification between soybean oil and methyl stearate. The experiment carried out using potassium-doped alumina (KNO_3/Al_2O_3). The solid basic catalyst was prepared with KNO_3 loading of 35% on alumina support and calcined at 700 °C. The highest ester yield obtained was 50.6% [9].

Battistel and co-workers [10] have investigated the reaction between the interesterification of tributyrin and methyl acetate, in the presence of heterogeneous basic catalysts typically used in the transesterification of triglycerides with alcohol process. The different kinetics could be attributed to a different reaction mechanism. For the reaction of interesterification it has been proposed a reaction mechanism associable to two coupled reactions of transesterification [21].
Figure 3.5, shows the interesterification base catalysed reaction mechanism, proposed as two transesterification reactions coupled.

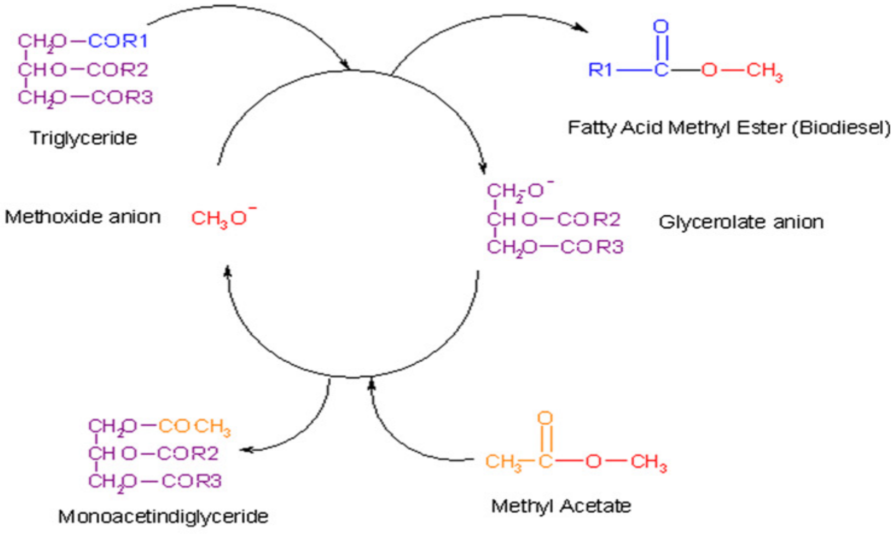
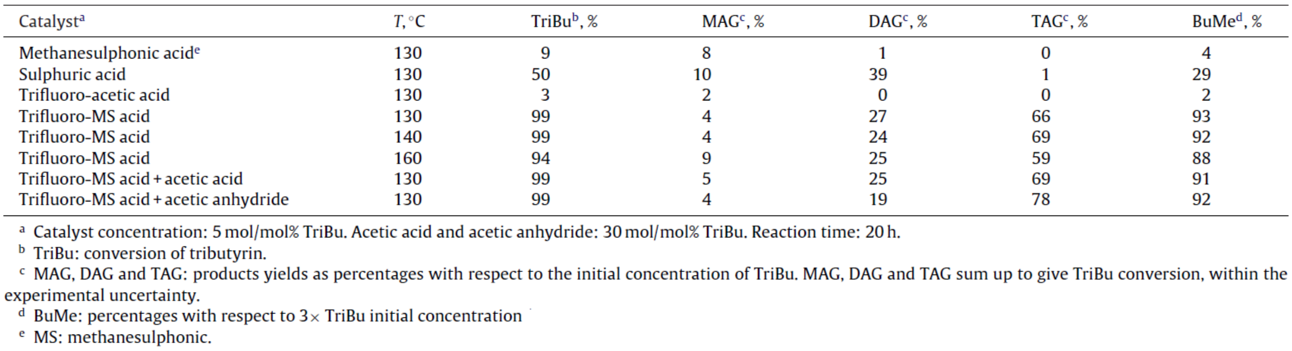


Figure 3.5. Alcohol and acid group exchange during interesterification of triglycerides with methyl acetate in presence of basic catalyst [20].

3.3.2 Acid catalyst

In the literature, there are few studies on the interesterification of oil with methyl acetate using acid catalysts. A study of tributyrin and methyl acetate compares homogeneous and heterogeneous acid catalysts [10]. The figure 3.6 shows the homogeneous acid catalysts used and the yields obtained.



Catalyst[a]	T, °C	TriBu[b], %	MAG[c], %	DAG[c], %	TAG[c], %	BuMe[d], %
Methanesulphonic acid[e]	130	9	8	1	0	4
Sulphuric acid	130	50	10	39	1	29
Trifluoro-acetic acid	130	3	2	0	0	2
Trifluoro-MS acid	130	99	4	27	66	93
Trifluoro-MS acid	140	99	4	24	69	92
Trifluoro-MS acid	160	94	9	25	59	88
Trifluoro-MS acid + acetic acid	130	99	5	25	69	91
Trifluoro-MS acid + acetic anhydride	130	99	4	19	78	92

[a] Catalyst concentration: 5 mol/mol% TriBu. Acetic acid and acetic anhydride: 30 mol/mol% TriBu. Reaction time: 20 h.
[b] TriBu: conversion of tributyrin.
[c] MAG, DAG and TAG: products yields as percentages with respect to the initial concentration of TriBu. MAG, DAG and TAG sum up to give TriBu conversion, within the experimental uncertainty.
[d] BuMe: percentages with respect to 3× TriBu initial concentration
[e] MS: methanesulphonic.

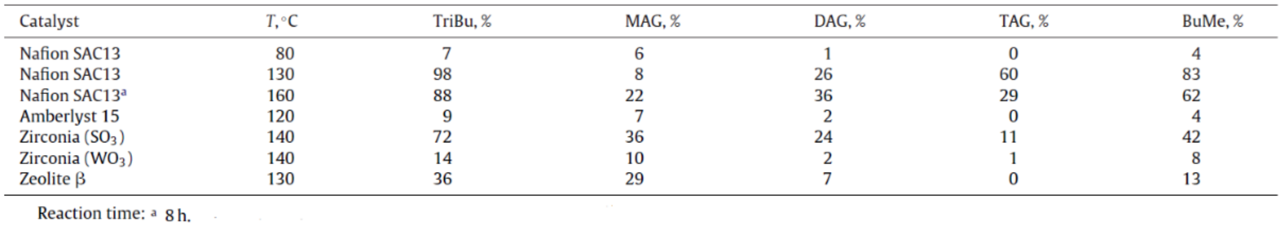
Figure 3.6. Yield esters (BuMe), triacetin (TAG) and intermediates (DAG, MAG) for interesterification of tributyrin and methyl acetate in the presence of homogeneous catalysts. Experiments carried out at a temperature between 130 °C and 160 °C for a time of 20 hours. The molar ratio between the reactants is equal to 40, the molar catalyst to oil ratio is 0.05 [10].

The highest yields were obtained with the trifluoromethanesulphonic acid at a temperature of 130 °C and after 20 hours of reaction. According to this study the conversion of the triglyceride and the yield of esters is approximately proportional to the acid strength of the used catalyst: acetic acid < methanesulphonic acid < sulphuric acid << trifluoromethanesulphonic acid.

The decisive step in the reaction mechanism in the presence of an acid catalyst is considered to be the interaction between this and the carbonyl oxygen of the ester. Therefore, the increase of the acid strength increases the interaction with the oxygen of the carbonyl and therefore increase the yields.

Phenyl-sulfonic acid-functionalized SBA-15 acid catalysts have been also tested for the preparation of biodiesel through the interesterification of extra virgin olive oil with ethyl acetate (molar ratio acyl donor/oil 20) leading to triglyceride conversion of 48% after 6h at 130 °C using catalyst loading of 30% w/w referred to the oil quantity [11].

Others results obtained with acidic heterogeneous catalysts are show in Figure 3.7.



Catalyst	T, °C	TriBu, %	MAG, %	DAG, %	TAG, %	BuMe, %
Nafion SAC13	80	7	6	1	0	4
Nafion SAC13	130	98	8	26	60	83
Nafion SAC13[a]	160	88	22	36	29	62
Amberlyst 15	120	9	7	2	0	4
Zirconia (SO_3)	140	72	36	24	11	42
Zirconia (WO_3)	140	14	10	2	1	8
Zeolite β	130	36	29	7	0	13

Reaction time: [a] 8 h.

Figure 3.7. Yield esters (BuMe), triacetin (TAG) and intermediates (DAG, MAG) for interesterification of tributyrin and methyl acetate in the presence of homogeneous catalysts. Experiments carried out at a temperature between 80 °C and 160 °C for a time of 20 hours. The molar ratio between the reactants is equal to 40, the molar catalyst to oil ratio is 0.05 [11].

The best results were obtained with the Nafion SAC-13, consisting of perfluorinated and sulfonated polymer chains dispersed on a silica support. It is the equivalent of the acid heterogeneous catalyst trifluoromethanesulphonic acid, previously seen. Also in this case, this active species provide high yields of esters and triacetin. The high activity of the Nafion is caused by the sulfonic groups contained in the fluorinated chains that have a length such as to allow the sulfonic groups to react in a manner similar to a homogeneous catalyst in solution.

The Amberlyst 15 resin is a polymer containing a high concentration of sulphonic groups. The equivalent homogeneous catalyst is the methanesulfonate acid, which showed a low catalytic activity. The Amberlyst 15 also shows a weak activity for the reaction of interesterification with heterogeneous catalysis.

Zirconia and zeolite are considered strong acids and are also used in the transesterification process. Despite their known acid strength, these catalysts gave low activity when they were employed for the interesterification process. In particular, the zirconia showed a higher catalytic activity compared to the zeolite due to the different size of the pores. The zirconia in fact has the largest pore size that allows a faster diffusion of the reactants inside the catalyst.

3.4 Enzymatic Interesterification

Selected enzymes also known as lipases are capable of catalysing the reaction of transesterification and interesterification. The catalysis takes place in mild conditions on different types of substrate.

The most important enzyme used for the interesterification of oil with methyl acetate is Candida Antarctica. This enzyme has been studied in different operating conditions always providing high biodiesel yields.

The choice of the reaction temperature (ranges from 30 to 50 °C) is a compromise between the operational stability of the lipase and the reaction rate of enzymatic interesterification.

Methyl acetate to oil molar ratio is important to determine the equilibrium composition, but problem associated with the enzyme inhibition was found with methyl acetate/oil molar ratio over 12/1. Good results were obtained by conducting the reaction of interesterification of soybean oil with methyl acetate with the enzyme Novozym 435 [12], as show in figure 3.8.

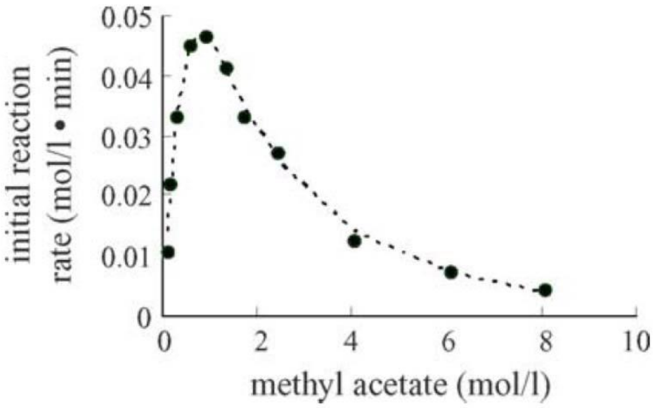


Figure 3.8. Interesterification reaction of soybean oil and methyl acetate with enzymatic catalysed. Reaction conditions: 10 g mixture of soybean oil and methyl acetate, 0.5 g Novozym 435, 40 °C, 150 oscillations/min [12].

The initial reaction rate increased with the concentration of methyl acetate till to a maximum, when more methyl acetate was added to this reaction, the initial reaction rate decreased gradually. The reduction in initial reaction rate was attributed to the inhibition of methyl acetate.

Talukder and co-workers studied the reaction of interesterification of palm oil and methyl acetate with Novozym 435 loaded at different concentrations. They found that an increase in the enzyme loading leads to faster reaction (see Figure 3.9) [13].

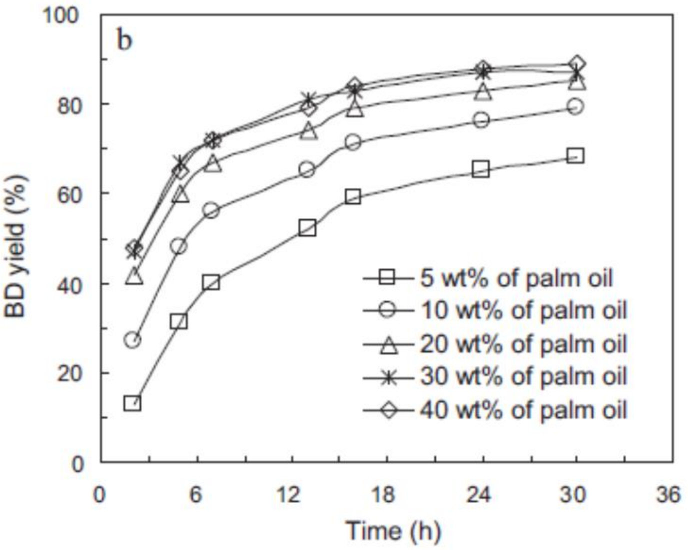


Figure 3.9. Effect of Novozym 435 loading on interesterification reaction using palm oil and methyl acetate. Reaction condition: T = 50 °C and methyl acetate/oil molar ratio = 12/1 [13].

Compared to the supercritical and chemically catalyzed interesterification, the use of lipases has significant advantages, because it is possible to obtain high-purity products by conducting the reaction in mild conditions. The main disadvantage for the industrialization of this process is the enzyme cost and the low durability of the catalyst. The problems related to the recovery of the catalyst can be reduced through the development of new lipase, and optimizing the immobilization on solid supports but no economic sustainable solution is currently available.

3.5 Supercritical Interesterification

The reaction of interesterification with methyl acetate can be conducted under supercritical conditions without any catalyst, similarly to transesterification in supercritical alcohol.

Several studies have investigated the conversion of various triglycerides and methyl acetate at a temperature comprised between 320 °C and 400 °C. Studies have shown that the yield of biodiesel grows proportionally to the temperature [14, 15]. However, increasing the temperature has always a positive effect on the yield in biodiesel. Saka found that exceeding 380 °C the yield tends to decrease due to the decomposition of unsaturated fatty acids into smaller fragments [5]. Even triacetin at high temperature undergo thermal decomposition [16]. The treatment time usually varies from 20 to 60 minutes, to achieve almost total conversions. One study in the literature shows that the reaction of interesterification in supercritical methyl acetate must be carried out at high molar ratios between the reagents and oil and high pressures to achieve high conversions [14]. A molar ratio of methyl acetate to oil equal to 42 and a pressure of 20 MPa are usually applied in these processes.

The Figure 3.10 shows the variation of the yield of only methyl esters (FAME) and the cumulative yield of esters and triacetin (FAME + TA) as a function of reaction time at temperatures in the range 300-380 °C. The experiments were conducted using a molar ratio methyl acetate to oil of 42/1 in 20 MPa.

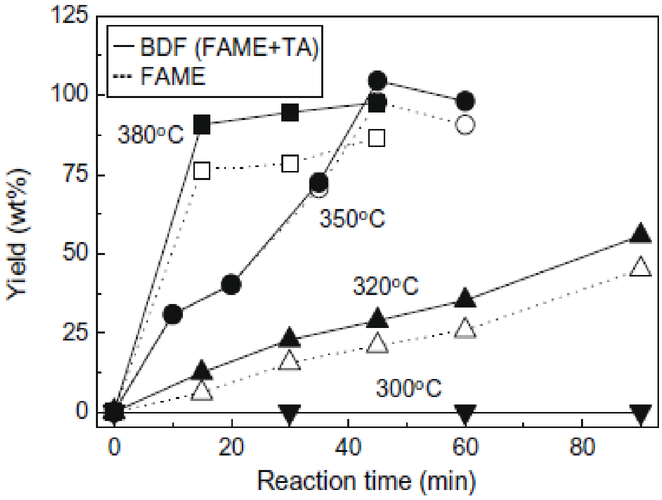


Figure 3.10. Results of FAME and BDF (FAME+TA) as function of time and temperature in 20 MPa pressure, molar ratio methyl acetate / rapeseed oil of 42/1 [5].

It must be noted that below 320 °C the reaction does not occur and that increasing the temperature of the reaction rate it rapidly increases. The reaction carried out at 380 °C is faster than that carried out at 350 °C, but the maximum attainable yield is lower. At 380 °C, also an high reaction time can cause a loss of biodiesel recovery. This result was attributed by the authors to the thermal decomposition of synthesized FAME. Especially, they noted that the distribution of fatty acids varied: the fatty acids containing unsaturation in the chain quickly decreased with increasing severity of the operating conditions. Therefore, the thermal decomposition on the unsaturation causes a decrease in yield of esters.

The supercritical process with methyl acetate can also be used with oils having high concentration of water and free fatty acids such as waste oils, without a reduction in the yield of biodiesel [15]. Through a reaction of esterification, the fatty acids can react with methyl acetate to form acetic acid and FAME, as shown in the following reaction:

$$\underset{\text{Fatty acid}}{RCOOH} + \underset{\text{Methyl acetate}}{CH_3COOCH_3} \longrightarrow \underset{\text{FAME}}{RCOOCH_3} + \underset{\text{Acetic acid}}{CH_3COOH}$$

In Figure 3.11 are presented the results of the supercritical interesterification of oleic acid with methyl acetate (molar ratio methyl acetate to oleic acid 12/1) performed at 20 MPa pressure and at different temperatures. For temperatures of 350 °C 10 minutes of treatment are enough to achieve very high yields, while at lower temperatures more than one hour of treatment is required [5].

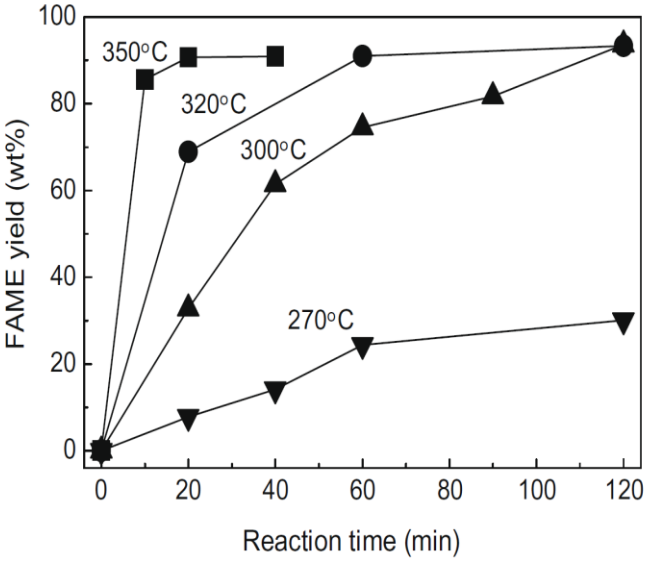


Figure 3.11. Results in the yield of esters as function of time and temperature in 20 MPa pressure, molar ratio methyl acetate / oleic acid of 12/1 [5].

The main disadvantages of the supercritical interesterification process are the installation costs and energy costs due to high temperature and pressure. As well, the use of high molar ratios among the reactants leads to an increase of the cost of separation.

3.6 Experimental section

3.6.1 Materials

The origin and composition of rapeseed oil used as a reactant in this study has been described in the previous chapter. Even the standards for the analytical procedure and the catalysts are identical to those already listed. For this study methanol was replaced by methyl acetate (HPLC grade> 99.8%)

purchased from Carlo Erba Reagents and triacetin (99%) was purchased from Sigma-Aldrich and used to calibrate the GC.

3.6.2 Reaction system and analytical techniques

For all experiments a stirred batch reactor with controlled temperature was used. For more details on the experimental system and the loading and reaction procedure, see the previous chapter. The concentrations of alkyl esters and triacetin in the samples were measured using a Agilent 7890B Gas Chromatograph (GC) equipped with a RESTEK Superchrom FAMEWAX capillary column (length 30 m, external diameter 0.32 mm, internal diameter 0.25 mm) using a Flame Ionization Detector (FID) and helium 5.0 as carrier gas, by the same method used for the analysis of products obtained by transesterification. Calibration was accomplished for fatty acid methyl esters (FAMEs) and triacetin (TA) by preparing solutions of known concentration of pure alkyl esters (C 16:0, C 18:0, C 18:1, C 18:2, C 18:3) and triacetin, using methyl heptadecanoate as internal standards. The standard solution was prepared by dissolving the internal standard in methyl acetate at concentrations close to the concentration of the other methyl esters.

Cumulative yields in fatty acid methyl esters Y_{FAME} and in triacetin Y_{TA} were computed according to the following formulas:

$$Y_{FAME} = \frac{M_{FAME}}{W^0_{Oil}} \qquad\qquad Y_{TA} = \frac{M_{TA}}{W^0_{Oil}}$$

where M_{FAME} and M_{TA} are the mass of free fatty acid methyl esters and triacetin determined from the GC calibration and W^0_{oil} is the initial mass of rapeseed oil loaded in the reactor.

It must be observed that the highest possible values of Y_{TA} and Y_{FAME} assuming complete conversion of triglycerides can be 24.7% and 100.4% considering the average molecular weight of the oil, methyl esters and triacetin of 881.8 g/mol, 295.28 g/mole and 218.2 g/mole respectively. Selected liquid samples were analysed by a BRUKER ARTAX diffuse wavelength X-ray Fluorescence (XRF) spectrophotometer, in order to verify the presence of tin ion dissolved in the solution.

Structural characterization of tin II oxide powder was performed by recording the powder X-ray diffraction (XRD) patterns using a Panalytical Empyrean diffractometer equipped with Cu Kα radiation (40 kV, 40 mA). The powders were scanned in the range 15–60◦ (2θ) with a scanning rate of 0.05 step/sec.

The morphology, microstructure and chemical composition of tin II oxide samples were investigated using a FEG-ESEM microscope (QUANTA 200), equipped with Energy Disperse Spectroscopy (EDS) probe.

3.7 Results and Discussion

3.7.1 Preliminary tests

Similarly as done for the transesterification process, the catalysts available in acidic behaviour was also used for the reaction of interesterification of rapeseed oil with methyl acetate. The majority of the experiments was carried out in the reactor by loading 1.88 g of rapeseed oil, 6.34 g of methyl acetate and 0.2 g of catalyst. Zirconium tungstate ($Zr(WO_4)_2$), niobium phosphate ($NbPO_4$), and tin (II) oxide (SnO) were tested for the reaction of interesterification and the results summarized in Figure 3.12. All experiments were carried out at the temperature of 483 K and an hour of treatment.

A blank catalyst free test was conducted at 483 K for one hour of treatment. Under adopted conditions we found FAME yields lower than 0.5% and no detectable amount of TA so that we can conclude that the interesterification of rapeseed oil does not take place in the absence of catalyst at this temperature.

Catalyst	Mass ratio catalyst /oil [g/g]	Molar ratio methyl acetate /oil [mol/mol]	**Y_{FAME} [% w/w]**	**Y_{TA} [% w/w]**	**Note**
-	0.0	40	0.5	0.0	Catalyst free test
SnO	0.1	40	60.8	5.9	
$Zr(WO_4)_2$	0.1	40	3.9	0.1	
$NbPO_4$	0.1	40	14.0	0.7	
SnO	-	-	-	-	1° leaching step
-	-	40	1.7	0.0	2° leaching step

Figure 3.12. Preliminary tests and leaching test of interesterification of rapeseed oil with methyl acetate in presence of heterogeneous catalysts. Operative conditions: temperature 483 K, time reaction 1 h.

The FAME yield found for $Zr(WO_4)_2$ catalysts and $NbPO_4$ were 3.9 % and 14.0% respectively, so we can conclude that these catalysts have a low activity for the studied reaction. Even for the interesterification reaction the SnO catalyst is the best among the tested catalysts, in fact, under the same operating conditions FAME yield of 60.8% and TA yield of 5.9% were obtained.

To exclude the possibility that soluble active species released by catalyst leaching can affect the reliability of collected experimental results we performed two consecutive run tests. First 6.35 g of methyl acetate and 200 mg of catalyst were loaded in the reactor and heated at 483 K for 1 hour. At the end of this first treatment step the liquid was recovered and carefully filtered to remove the tin (II) oxide powder. In a second test the recovered methyl acetate was mixed with 1.88 g of oil and the mixture was loaded into the clean reactor. This mixture was heated at 483 K for 1 hour and, after cooling, it was analysed by GC. Estimated Y_{FAME} was the same as in the catalyst free test and it was accompanied by no detectable amount of triacetin. These data confirm that leaching of active species cannot affect the experimental results under adopted operative conditions.

The XRF analysis obtained by interesterification of rapeseed oil with methyl acetate catalysed by SnO was performed to confirm the absence of tin in solution. The XRF analysis showed that the catalyst is not soluble in the biodiesel (see figure 3.13).

Figure 3.13. XRF analysis of liquid biodiesel mixture obtained of interesterification of rapeseed oil with methyl acetate catalysed by SnO: analysis confirm the absence of tin in solution.

3.7.2 Effect of the reaction temperature and of the methyl acetate to oil molar ratio

The interesterification of rapeseed oil with methyl acetate was studied as a function of the reaction temperature using a fixed molar ratio of methyl acetate to oil of 40 and a ratio of catalyst to oil 0.65 mol/mol. The obtained results are shown in Figure 3.14.

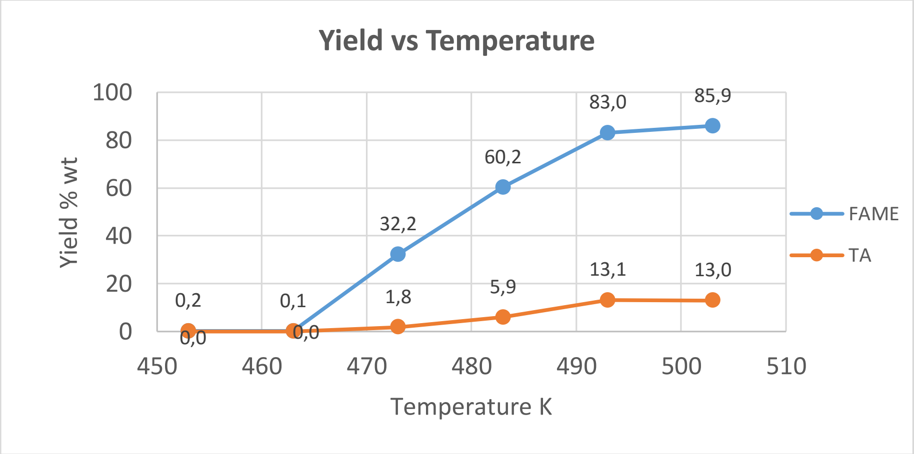


Figure 3.14. Interesterification of rapeseed oil with tin oxide using methyl acetate: effect of the catalyst as a function of the reaction temperature. Molar ratio methyl acetate to oil = 40 and catalyst to oil = 0.65; reaction time 1 hour.

Experiments performed below 463 K gave very low conversion. Increasing the reaction temperature to 473 K yields of methyl esters and triacetin was 32.2% and 1.8 % respectively. These results indicate that the tin oxide catalyst needs a minimum temperature to be active in the reaction. When the temperature was increased to 483 and 493 K, FAME yields increased to 60.2 % and 83.0 % respectively, while TA yields were 5.9% and 13.1% respectively. At higher temperature yield had a limited increment. The kinetics of the reaction, as expected, is favoured at elevated temperatures, while at temperatures lower than 463 K the catalyst appears not to be active.

Experiments in the presence of tin oxide at molar ratio catalyst to oil of 0.65 were carried out changing the molar ratio methyl acetate to rapeseed oil from 20 to 60 at 473 K with reaction times of 4 hours (see Figure 3.15). When the methyl acetate/oil ratio was increased from 20 to 40 the yield of methyl esters increased from 61.9 % to 92.2 %, while the TA yield was increased from 7.4

to 17.2% respectively. A further increase of the molar ratio at 60 leads to an increase in the yield of 20.4 % of triacetin while the yield of methyl esters remained practically constant.

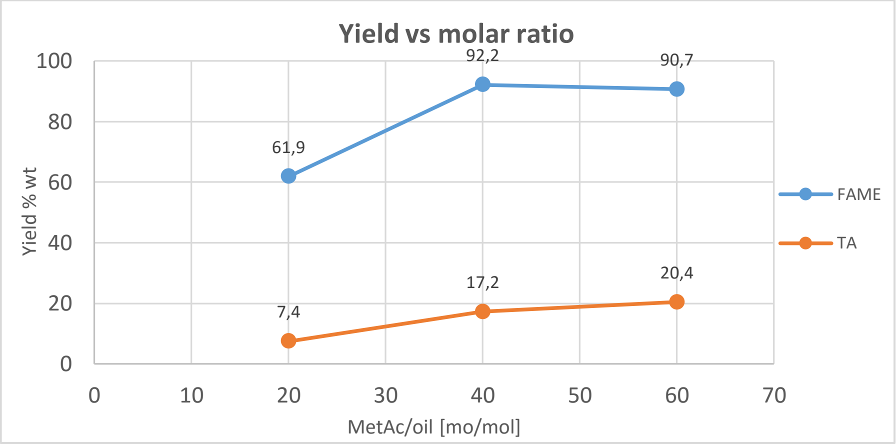


Figure 3.15. Interesterification of rapeseed oil with tin oxide using methyl acetate: effect catalyst as a function of the methyl acetate to oil molar ratio. Temperature 483 K, molar ratio catalyst to oil = 0.65, reaction time 4 hour.

Similarly to the transesterification, also in the interesterification reaction, increasing the ratio of acyl acceptor and oil is promotes the shift of each step of equilibrium reaction towards the products and therefore the yields increase.

3.7.3 Effect of the catalyst concentration and reaction time

The effect of the concentration of tin oxide catalyst has been studied for the reaction of interesterification of rapeseed oil. The tests were all carried out at the temperature of 483 K, one hour of treatment and with a molar ratio of methyl acetate to oil of 40 (see Figure 3.16).

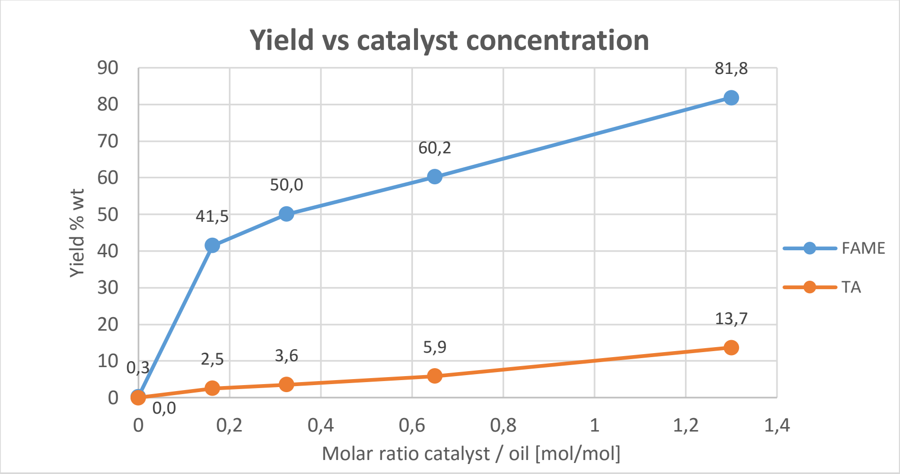


Figure 3.16. Interesterification of rapeseed oil with tin oxide using methyl acetate: effect of the catalyst concentration. Temperature 483 K, molar ratio methyl acetate to oil = 40, reaction time 1 hour.

A FAME yield of 41.5% was found when the molar ratio catalyst to oil was 0.16. When the catalyst /oil ratio was increased to 0.32 the yield of methyl esters was found 50.0 %, while the TA yield was 3.6%. When the molar ratio catalyst to oil was increased from 0.65 to 1.3 the yield of methyl esters increased from 60.2 % to 81.8 %, while the TA yield increased from 5.9% to 13.7% respectively. Increasing the concentration of catalyst, FAME and TA yields increased, this result was a clear indication of faster overall rate of reaction.

The reaction of interesterification of rapeseed oil with methyl acetate in the presence of tin oxide was studied varying the reaction time. This parameter was varied from 0.5 to 4 hours, using a temperature of 483 K, a molar ratio of methyl acetate to oil of 40 and a molar ratio of catalyst to oil of 0.65 for all tests (Figure 3.17).

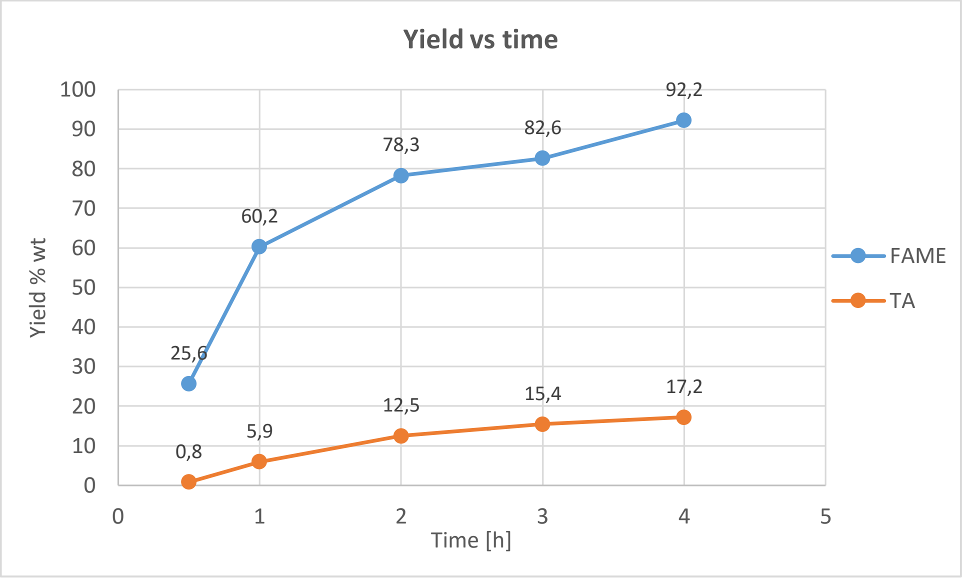


Figure 3.17. Interesterification of rapeseed oil using tin oxide: effect of the reaction time. Temperature 483 K, initial molar ratio of methyl acetate to oil = 40, molar concentration catalyst to oil = 0.65.

When the reaction time was increased from 0.5 to 1 h, FAME yields were 25.6 and 60.2% respectively, while TA yields were 0.8% and 5.9%. Increasing the treatment time at 2 and 3 hours, the FAME yield increased from 78.3% to 82.6% and TA yield increased from 12.5 to 15.4% respectively. A further increase of the reaction time from 3 hours to 4 hours causes an increase of the conversion: the yield of FAME reaches 92.2% while the TA yield obtained was 17.2%.

3.7.4 Effect of the presence of water as impurities

An important positive property of the catalyst would be a good resistance against water action whose presence is usually detrimental for the catalyst activity. The water is a component that may be present in vegetable oil emulsion even in concentrations of about 350 mg per kg of oil [6], while for the exhausted oils the amount of water could be much higher. It is known that the water can be a powerful poison especially for chemical species that have an acidic or basic behaviour. We have investigated the behaviour of the SnO catalyst carrying out experiments by adding water to the reaction.

In the presence of water concentration of 2.1 % w/w with respect to the mass of oil, the yield of methyl esters was unexpectedly higher than the yield obtained without added water. A comparison between the obtained results is shown in Figure 3.18.

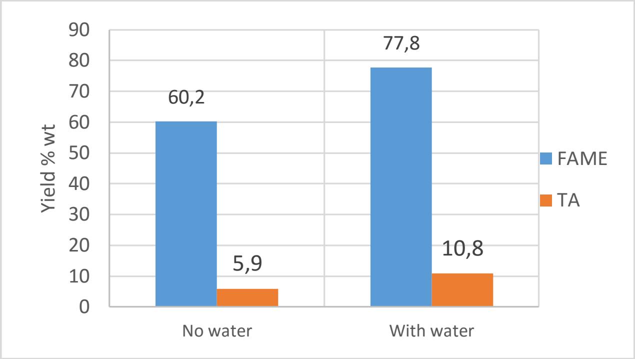


Figure 3.18. Interesterification of rapeseed oil using tin oxide with in the presence of water 2.1% w/w with respect to the mass of oil. Temperature 483 K, initial molar ratio of methyl acetate to oil = 40, molar concentration catalyst to oil = 0.65, reaction time 1 hour.

These results can be explained assuming that hydrolysis of methyl acetate can take place in the presence of water leading to the formation of acetic acid and methanol. The reaction is known as hydrolysis of the methyl acetate and is written as follows:

$$CH_3COOCH_3 + H_2O \xleftrightarrow{H^+} CH_3OH + CH_3COOH$$

The hydrolysis is an equilibrium reaction [18]. The methanol product may react with the triglyceride in a transesterification reaction [19]. As reported in the literature the transesterification reaction has a faster kinetic compared to that of the interesterification and this could be related to the higher obtained yields.

This hypothesis is supported by the fact that the analyses of the products of these experiments showed the presence of two new compounds that are probably diacetin and monoacetin, in addition to the triacetin. The standards of these compounds are currently not available and therefore we can only speculate that the transesterification with methanol and the interesterification with methyl acetate are reactions that take place in parallel in the same reactor.

We then synthesized the diacetin and the monoacetin in the laboratory, starting from the compound triacetin available as high purity. It has been carried out the transesterification of triacetin with methanol using sodium methoxide as the catalyst. For the stoichiometry of the reaction the molar ratio between methanol and triacetin should be 3 to 1; anyway often an excess of alcohol is used to obtain high conversions. In our experiment, to prevent the complete conversion of triacetin a lower molar ratio of methanol to triacetin was used to allow formation of the monoacetin and diacetin.

Gas chromatographic analysis showed the same signals previously attributed to diacetin and monoacetin.

Moreover both the oil and the methyl acetate were dried with molecular sieves to remove water: the methyl acetate had a water content of 500 mg / kg while the oil had 300-450 mg / Kg.

When the oil mass was dried the diacetin and monoacetin signals decreased compared to those recorded in tests in which wet chemicals were used. In figure 3.19 it is shown a comparison under the same operating conditions, between the dry (Figure 3.19b) and wet (Figure 3.19a) tests in which the normal procedures and the test in which water was added to the reaction have been performed and the oily mass was dried.

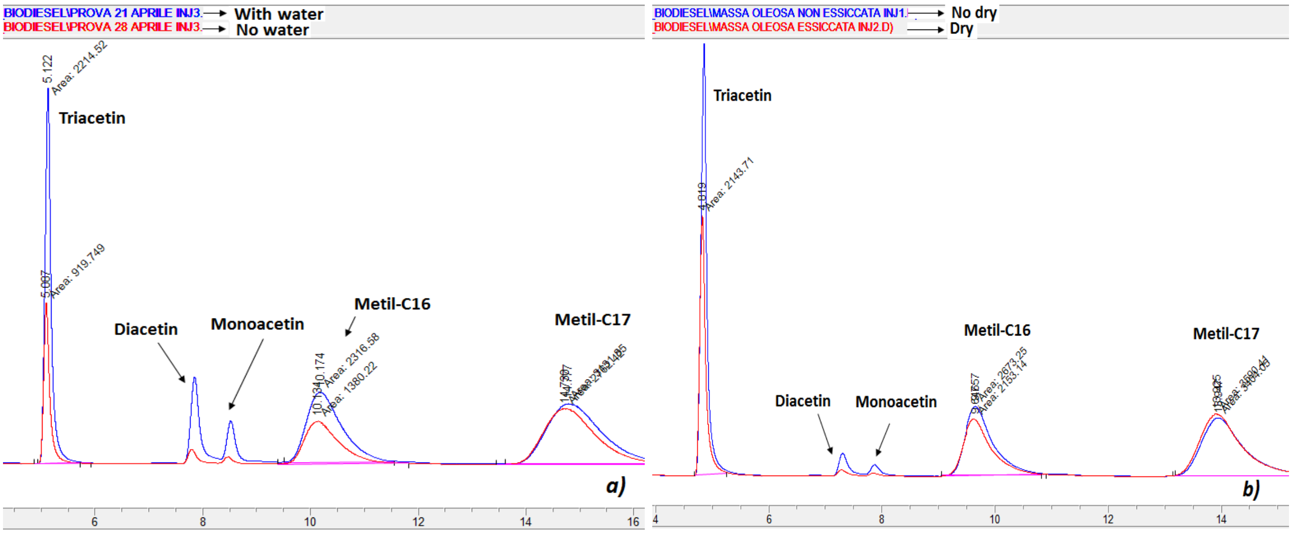


Figure 3.19. Comparison of chromatograms between test with addition of water in the reactor and test in the absence of water in the reactor (a), and between the test in which the reactants were dried and the test in which the reactants were not dried (b) .

Moreover it was observed a small decrease in methyl ester yields when the oil was dried. This result confirms that the hydrolysis of methyl acetate is carried out and the methanol that is generated participates in the reaction favouring the global kinetics of the process.

This explains the increase in the yield of methyl esters, diacetin and monoacetin. The increase in the yield of triacetin, instead, can be rationalized considering that the acetic acid can react with glycerol (or with the -OH groups of diacetin and monoacetin). The esterification reaction between acetic acid and glycerol is an equilibrium reaction which leads to the formation of monoacetin, diacetin and triacetin [22]. The reaction is shown schematically in Figure .20.

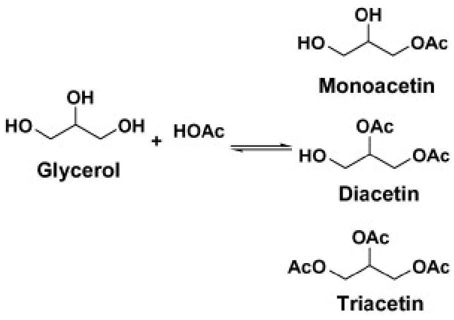


Figure 3.20. Esterification reaction of glycerol with acetic acid to form monoacetin, diacetin and triacetin [22].

The esterification of glycerol with acetic acid itself increases the concentration of monoacetin and diacetin, as well as increase the yield of triacetin. As all the reactions of esterification is catalysed by acids or bases and it is plausible to think that SnO acts as a catalyst for this reaction. The reaction of esterification of glycerol with acetic acid could explain also the absence of glycerol in the reaction products.

In any case, here it is important to note that despite the presence of high water concentration, the catalyst continues to have excellent performance.

3.7.5 Catalyst characterization and reuse of catalyst

Some analyses for the characterization of the heterogeneous solid catalyst have been undertaken and are presented in this paragraph.

The X-ray diffraction patterns of the tin II oxide samples are shown in Figure 3.21. Image a) show a SnO catalyst unmilled, image b) show the SnO milled with laboratory mortar and image c) represents the SnO powder (milled with laboratory mortar) after the interesterification process. The XRD analysis on samples of tin oxide are equal to each other. The narrow and high signal indicates that the analysed material has high crystallinity. The overlap with the database indicates that only tin II oxide is present in the samples, and there are no other components.

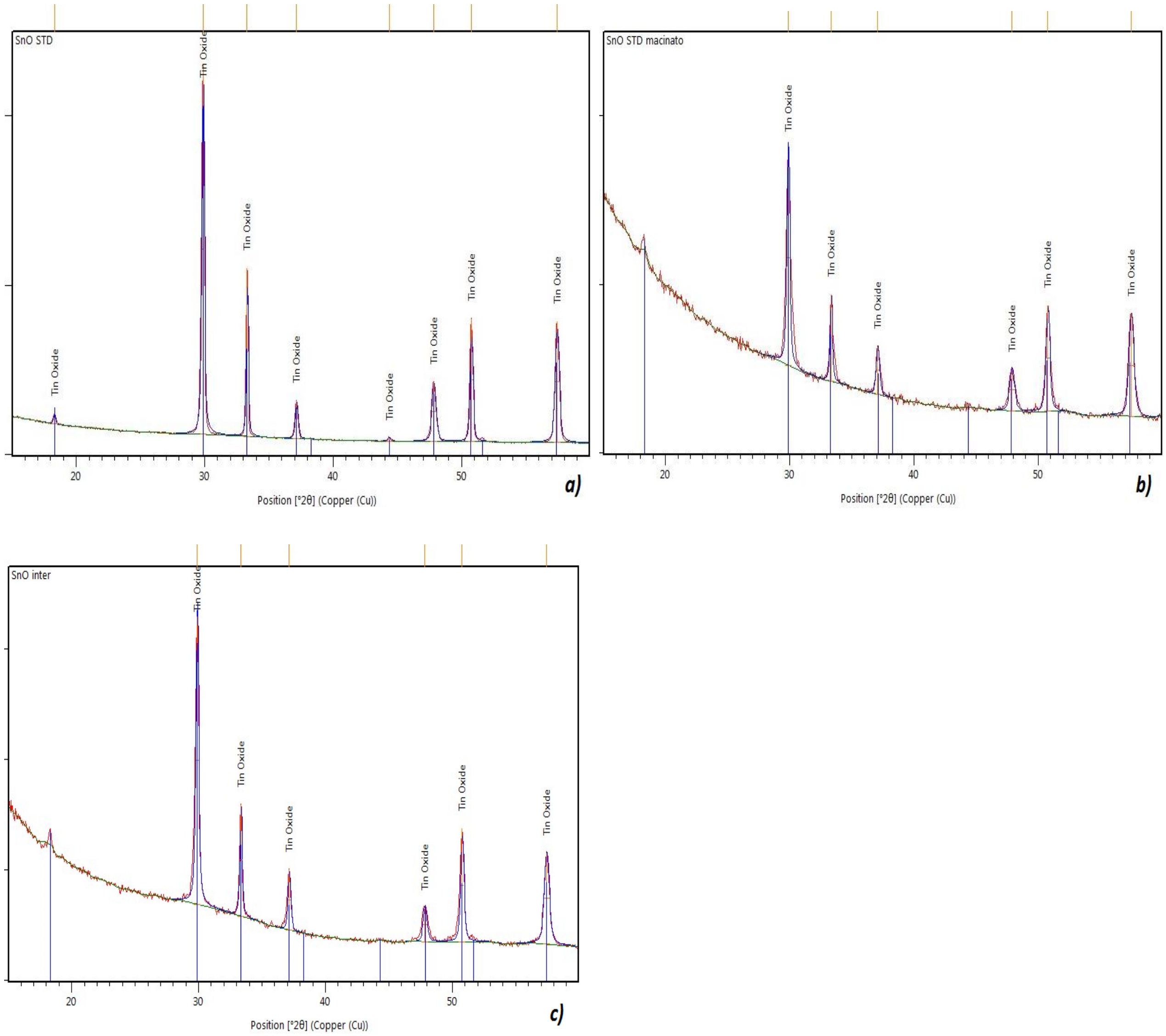


Figure 3.21: XRD patterns of tin(II) oxide, 99.9% Alfa Aesar powder (SnO), a) unmilled and not used, b) milled with laboratory mortar and not used, c) milled with laboratory mortar and used for a interesterification process.

Another particularly important parameter for the heterogeneous catalysis is the reusability of the catalyst. The SnO catalyst was reused three times and the products obtained for each cycle analysed (see Figure 3.22). For each test, the catalyst was collected and washed with methyl acetate before recycle. The experiments carried out under the same operating conditions (temperature 483 K, molar ratio methyl acetate to oil 40, molar ratio catalyst to oil 0.65 and reaction time 1 hour) gave a yield unexpectedly higher in subsequent cycles. The second use onward, the catalyst had a steady performance.

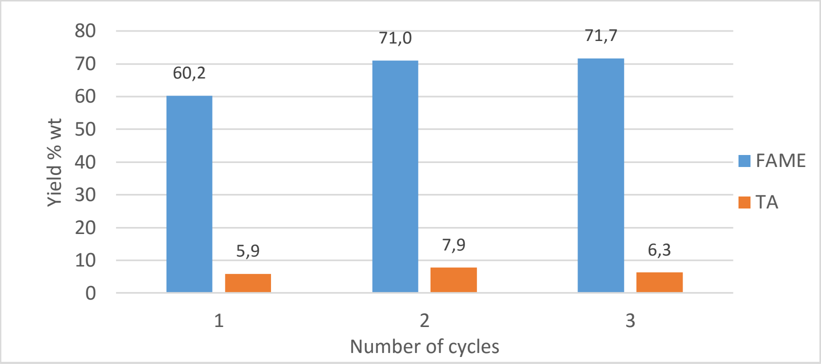
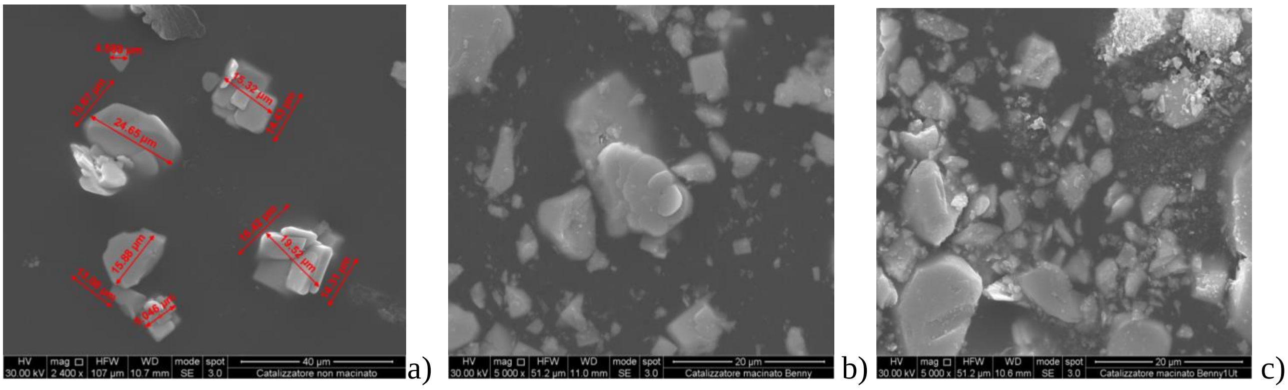
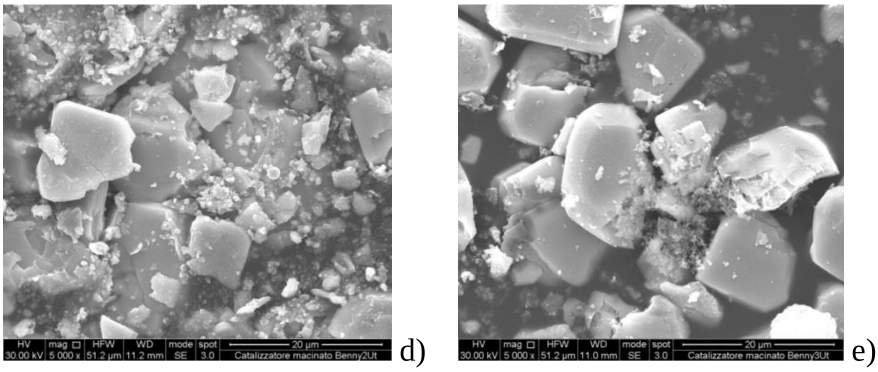


Figure 3.22. Interesterification of rapeseed oil using tin oxide reused several times. Temperature 483 K, initial molar ratio of methyl acetate to oil = 40, molar concentration catalyst to oil = 0.65, reaction time 1 hour.

The increase in the yield can be explained assuming that after the first treatment the surface has undergone changes which increase the catalytic activity, as it appears in the SEM images obtained on the catalyst before and after its use.

Figure 3.23 reports SEM micrographs of the different samples. Image a, show SnO unmilled, in which large and regular particles appear. Image b shows when SnO is milled with mortar laboratory in which one can see tiny fragments of irregular shape. The other images, show the SnO catalyst after the first use (c), after two uses (d) and after three uses (e). For each use, the catalyst was placed in contact with the reagents for one hour at 483 K. From the pictures it seems that the catalyst changes its morphology with the reaction cycles, in fact, smaller fragments are formed that could lead to higher interfacial area.





d) e)

Figure 3.23. Representative SEM of tin (II) oxide, 99.9% Alfa Aesar powder (SnO), samples: unmilled and not used, b) milled with laboratory mortar and not used, c) milled with laboratory mortar and used for interesterification process.

For a better understanding of these results it would be necessary a specific investigation of the catalysts in terms of specific surface area, the crystal structure and acidic properties of the sites.

The grinding of the catalyst powder causes the increase of the surface and consequently a better catalytic performance, to other hands the formation of smaller fragments can make more expensive the stage of separation from the products. To meet these challenges and at the same time enhance the potential of SnO would be appropriate to use a catalytic support on which disperse the catalyst. The use of a support with a high specific surface area and with the typical particle size of the pellets may improve the performance of the catalyst system and at the same time make easier the recovery.

3.8 Conclusion

The tin (II) oxide was used to catalyze the reaction of interesterification of rapeseed oil and methyl acetate. The leaching tests and some XRF analysis of the mixture of products have shown that the tin oxide is a heterogeneous catalyst and that no species soluble in methyl acetate acts as a catalyst for the reaction of interesterification. High FAME yields were obtained for reactions carried out at a temperature between 473 and 503 K with a molar ratio of methyl acetate to oil equal to or greater than 40 and short time (1-4 hours).

Tin (II) oxide was found an effective catalyst for the production of biodiesel simple to recover, good resistance to water deactivation and reusable. These results would be interesting in the perspective of industrial utilization of the process because it would make possible the utilization of cheap feedstock such as waste cooking oil.

The characterization of the catalyst requires further investigation such as the surface area and acid strength of sites. The potential of the catalyst tin (II) oxide can be significantly increased in the case where high surface areas are generated. Therefore a more effective grinding or a synthesis method which allows to increase the specific area of the catalyst may improve the performance of tin (II) oxide.

REFERENCE

[1] Casas, A; Ramos, MJ; Perez, A. Production of Biodiesel through Interesterification of Triglycerides with Methyl Acetate, ISBN: 978-1-62808-565-5. Editor: David A. Sanders. © 2013 Nova Science Publishers, Inc.

[2] Voegele, E. Glycerin's Role in 2009. Biodiesel Magazine. December 2008.

[3] Bonet, J; Costa, J; Sire, R; Reneaume, JM; Pleşu, AE; Pleşu, V; Bozga, G. Revalorization of glycerol: Comestible oil from biodiesel synthesis, Food Bioprod. Process, 2009, 87, 171-178.

[4] Garcia, E; Laca, M; Perez, E; Garrido, A; Peinado, J. New Class of Acetal Derived from Glycerin as a Biodiesel Fuel Component, Energy Fuels, 2008, 22, 4274–4280.

[5] Saka, S. Isayama Y. A new process for catalyst-free production of biodiesel using supercritical methyl acetate, Fuel 2009, 88, 1307–1313.

[6] Casas, A; Ramos, MJ; Perez, A. Kinetics of chemical interesterification of sunflower oil with methyl acetate for biodiesel and triacetin production, Chem. Eng. J., 2011, 171 1324-1332.

[7] Galia, A; Centineo, A; Saracco G; Schiavo B; Scialdone O. Interesterification of rapeseed oil catalyzed by tin octoate, Biomass and Bioenergy, 2014, 27, 193–200.

[8] Xie, W; Qi, C. Interesterification of Soybean Oil and Lard Blends Catalyzed by SBA15-pr-NR3OH as a Heterogeneous Base Catalyst. J. Agric. Food Chem. 2013, 61, 3373−3381.

[9] Xie, W; Chen, J. Heterogeneous Interesterification of Triacylglycerols Catalyzed by Using Potassium-Doped Alumina as a Solid Catalyst. J. Agric. Food Chem. 2014, 62, 10414−10421.

[10] Battistel, E; Calaprice, C; Gualdi, E; Rebesco, E; Usai, EM. Co-production of butyrate methyl ester and triacetylglycerol from tributyrin and methyl acetate, Appl. Catal., A, 2011, 394, 149–157.

[11] Usai, E.M; Sini, M.F; Meloni, D; Solinas, V; Salis, A. Sulfonic acid-functionalized mesoporous silicas: Microcalorimetric characterization and catalytic performance toward biodiesel synthesis, Micropor. Mesopor. Mat., 2013, 179, 54–62.

[12] Xu, Y., Du, W., Liu, D.,. Study on the kinetics of enzymatic interesterification of triglycerides for biodiesel production with methyl acetate as the acyl acceptor. Journal of Molecular Catalysis B: Enzymatic 32 (5–6), 2005, 241–245.

[13] Talukder, MR; Das, P; Fang, TS; Wu, JC. Enhanced enzymatic transesterification of palm oil to biodiesel, Biochem. Eng. J.,2011, 55, 119–122.

[14] Campanelli, P; Banchero, M; Manna, L. Synthesis of biodiesel from edible, non-edible and waste cooking oils via supercritical methyl acetate transesterification, Fuel, 2010, 89, 3675–3682.

[15] Tan KT; Lee, KT; Mohamed, AR. A glycerol-free process to produce biodiesel by supercritical methyl acetate technology: An optimization study via Response Surface Methodology, Bioresour. Technol., 2010, 101, 965–969.

[16] Niza, N.M; Tan, Lee, K.T; Ahmad, Z . Biodiesel production by non-catalytic supercritical methyl acetate: Thermal stability study. Applied Energy, 2013, 101, 198–202.

[17] Casas, A; Ruiz, JR; Ramos, MJ; Perez, A. Effects of triacetin on biodiesel quality, Energy Fuels, 2010, 24, 4481-4489.

[18] Ehteshami, M.; Rahimi, N.; Eftekhari, A. A.; NASR, M. J. Kinetic study of catalytic hydrolysis reaction of methyl acetate to acetic acid and methanol, Iran. J. Sci. Technol., 2006, 30, 595-606.

[19] Casas, A; Ramos, MJ; Perez, A. New trends in biodiesel production: Chemical interesterification of sunflower oil with methyl acetate, Biomass Bioenergy, 2011, 35, 1702-1709.

[20] Methanol-enhanced chemical interesterification of sunflower oil with methyl acetate Abraham Casas, María Jesús Ramos, Ángel Pérez. Fuel 106 (2013) 869–872.

[21] Stanton, MG. 'New' catalysts for the ester-interchange reaction: The role of alkali-metal alkoxide clusters in achieving unprecedented reaction rates, J. Am. Chem. Soc., 1998, 120, 5981-5989.

[22] V. L.C. Gonçalves, B. P. Pinto, J. C. Silva, C. J.A. Mota. Acetylation of glycerol catalyzed by different solid acids, Catalysis Today, 2008, 133–135, 673–677.

Chapter 4

HYDROTHERMAL TREATMENT OF VEGETABLE OILS

4.1 Premise

This chapter shows results of the experimental activity carried out within the PhD course during a research period spent at the Institute of Catalysis Research and Technology (IKFT) at the Karlsruhe Institute of Technology Karlsruhe (KIT), Germany, from January 2016 to July 2016.

The topic of this activity was the study of the conversion of vegetable oils into biofuels by hydrothermal process in the presence of heterogeneous catalysts.

Rapeseed oil was treated in water at temperatures of 325-375 °C for treatment times of between 15 minutes and 120 minutes. Catalysts based on nickel and zirconia oxide were used to promote the reactions.

Glycerol and stearic acid were also used as model compounds of the vegetable oil to facilitate the interpretation of the analysis results.

The experiments were carried out in batch reactors and all the product phases obtained with process were analysed by chromatographic techniques. In particular, the water-soluble products, the liquid organic fraction and the gas were characterized.

The main focus of the results was the organic liquid phase obtained via deoxygenation of stearic acid, and the in situ production of hydrogen from glycerol and water.

The best operating conditions to maximize the parameters have been sought.

4.2 Introduction

As explained in the previous chapters, triglycerides can be converted into alkyl esters by esterification with acyl acceptor, and this route is used to produce biodiesel fuel on commercial scale [1, 2]. Alternatively, the esterification processes, some authors have proposed the catalytic cracking of the triglyceride in an inert environment in order to produce fuel. A brief description of the process is presented in section 4.3.

More recently, there has been interest in producing hydrocarbons from triglycerides, and this conversion can be done via heterogeneous catalytic reactions in a hydrothermal reaction medium [3]. A more appropriate use of triglycerides could providing a first hydrolysis step with water, to form free fatty acids and glycerol, and the subsequent stages of deoxygenation of fatty acids and generation of hydrogen gas from glycerol. These transformations can be carried out in the presence of water, for reasons that are indicated in the following paragraphs.

4.3 Cracking

Catalytic cracking is an alternative method for triglyceride upgrading to produce fuels, and it has been studied with various zeolite catalysts [4, 5].

The main products obtained from zeolite-catalysed cracking of triglycerides are linear and cyclic paraffins, olefins, and oxygenated compounds including aldehydes, ketones and carboxylic acids. Many reactions occur during this process: cracking, hydrolysis, isomerization, dehydrogenation, aromatization (Diels-Alder reaction) and coking. Figure 4.1 shows a proposed reaction mechanism for oil conversion [6].

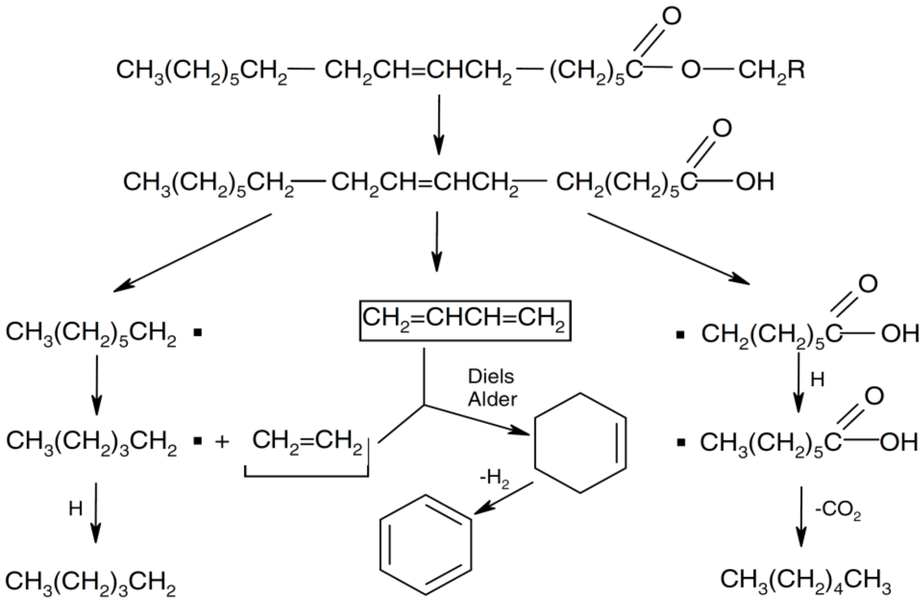


Figure 4.1. Mechanism for triglycerides cracking [6].

Normally, these reactions proceed through the formation of carbon ions or via a free radical mechanism. The products resulting from the cracking of oils produces low-quality fuels, as the oxygen in the feedstock remains in the products, thus resulting in a bio-oil with standards not in compliance with those required for suitable fuels. Furthermore, a high amount of aromatic compounds are formed, whose use is strictly regulated for environmental issues. The main problem, however, is that the cracking reactions using the catalysts (mainly zeolite) that are not selective towards the products of interest and produce a high amount of coke [7].

Typical used catalysts for the cracking process of vegetable oils are HZSM-5, HBeta and USY zeolites. They are used as a fixed bed inside a reactor and typical operating conditions are a temperature range of 350-450 °C and atmospheric pressure. Some authors reported zeolite conversion in petrol and gas products of 99%, 82% and 53% when HZSM-5, HBeta and USY catalysts, respectively, have been used. The selectivity toward gasoline production was instead of 28%, 22% and 7%, respectively [4]. An increase in the selectivity toward gasoline up to 40% can be obtained using mesoporous materials [5].

4.4 Hydrolysis of vegetable oils

Hydrolysis of oils/fats consists of three stepwise reactions: one molecule of triglyceride (TG) is hydrolysed to one molecule of diglyceride (DG) to produce one molecule of fatty acid (FA); then

DG is hydrolysed to monoglyceride (MG) which is further hydrolysed to glycerol; the three steps produce one molecule of glycerol and three molecules of FAs in total (see Figure 4.2). As a backward reaction (condensation), however, glycerol can react with a FA to give a MG; similarly MG and DG can return to DG and TG, respectively. In subcritical water, this hydrolysis and re-condensation reaction reactions occurs without any catalyst [8].

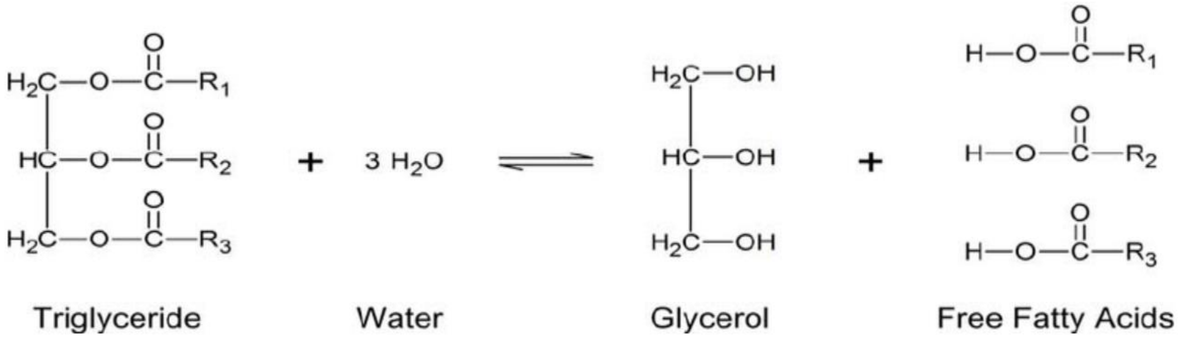


Figure 4.2. Hydrolysis of a triglyceride to glycerol and free fatty acids.

Figure 4.3 shows the yield of FA obtained from rapeseed oil in subcritical water at various temperature values. Although a higher temperature realized a higher rate of FA formation, the hydrolysis reaction reaches equilibrium at around 90% w/w yield of FA with a used volumetric ratio of water to rapeseed oil of 1/1 [8]. This incomplete result might be due to the backward reaction mentioned above. Under the conditions of 270 °C and 20 MPa, the yield of FA reached 90% w/w after 60 minutes. Increasing the temperature, the hydrolysis reaction becomes faster, reaching the maximum FAs yield in about 20 min at 320 °C.

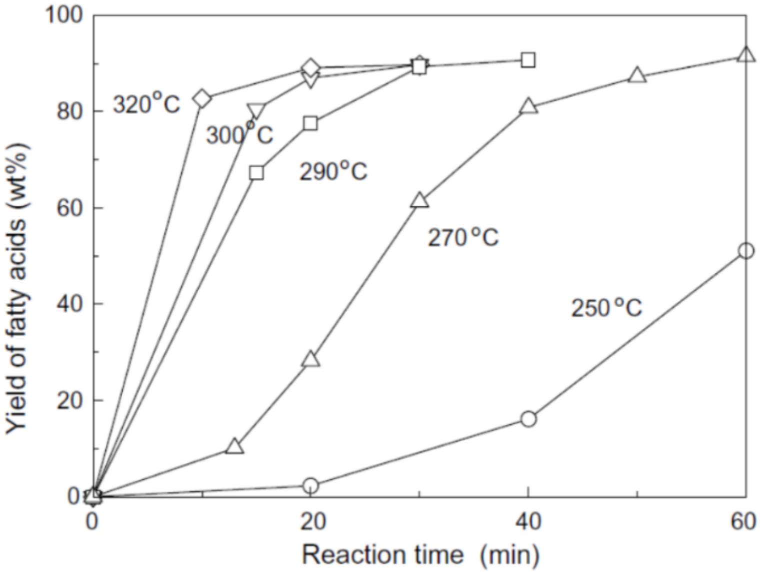


Figure 4.3. Hydrolysis of rapeseed oil (TG) to free fatty acids (FFAs) in subcritical water at 20 MPa and water/TG = 1/1 (v/v) [8].

4.5 Deoxygenation of fatty acids

Fatty acids and their derivatives are in general considered promising precursors for producing diesel and jet fuel range hydrocarbons. Oleaginous microbes, including algae, yeast, and fungi, are receiving increasing attention for use in fatty acid production [9,10]. However, as mentioned, the use of fatty acids and their derivatives as fuel is limited by their high oxygen content, which leads to a low heating value, as well as a high cloud and pour points [3, 11]. Decarboxylation is one of the possible route for the removal of oxygen from fatty acids [3, 11]. However, the general goal is to deoxygenate fatty acids, resulting in straight-chain hydrocarbons. Plausible reaction paths for production of linear hydrocarbons from fatty acids are illustrated below (Figure 4.4) [12].

The fatty acids can be converted into hydrocarbons by direct decarboxylation or decarbonylation: in the first case the carboxyl group releases carbon dioxide, and produces a linear alkane (I), in the second case the carboxyl group releases carbon oxide and water, forming a linear alkene (II). The decarbonylation reaction can take place by incorporating hydrogen to form alkane rather than alkene (III).

The production of linear hydrocarbons from fatty acids can be made by adding hydrogen, by direct hydrogenation. The direct hydrogenation reaction consists in the incorporation of hydrogen in the carboxylic acid group, forming alkane and water (IV) [12].

Liquid phase reactions			ΔG_{573} (kJ/mol)	ΔH_{573} (kJ/mol)
I.	Decarboxylation:	$\text{R-COOH} \longrightarrow \text{R-H} + CO_2\,(g)$	-83.5	9.2
II.	Decarbonylation:	$\text{R-COOH} \longrightarrow \text{R}'\text{-H} + CO\,(g) + H_2O\,(g)$	-17.0	179.1
III.		$\text{R-COOH} + H_2\,(g) \longrightarrow \text{R-H} + CO\,(g) + H_2O\,(g)$	-67.6	48.1
IV.	Hydrogenation:	$\text{R-COOH} + 3H_2\,(g) \longrightarrow \text{R-CH}_3 + 2H_2O\,(g)$	-86.1	-115.0

R = saturated alkyl group *R′ = unsaturated alkyl group*

Figure 4.4. Thermodynamic data for production of linear C17 hydrocarbons from stearic acid at 300 °C [12].

Due to biochemical process of synthesis fatty acids (of vegetable origin) are constituted by chains with an even number of carbons. The decarboxylation and decarbonylation reactions result in the loss of a carbon atom, generating a hydrocarbon chain with odd number. The hydrogenation reaction instead, is the only way that does not cause shortening of the chain and therefore leads to the formation of alkanes with even number of carbon atoms number.

Deoxygenation reactions can also take place with triglyceride rather than by free fatty acids. In this case, the hydrogenation (or hydrodeoxygenation) produces propane, hydrocarbons and water (Figure 4.5).

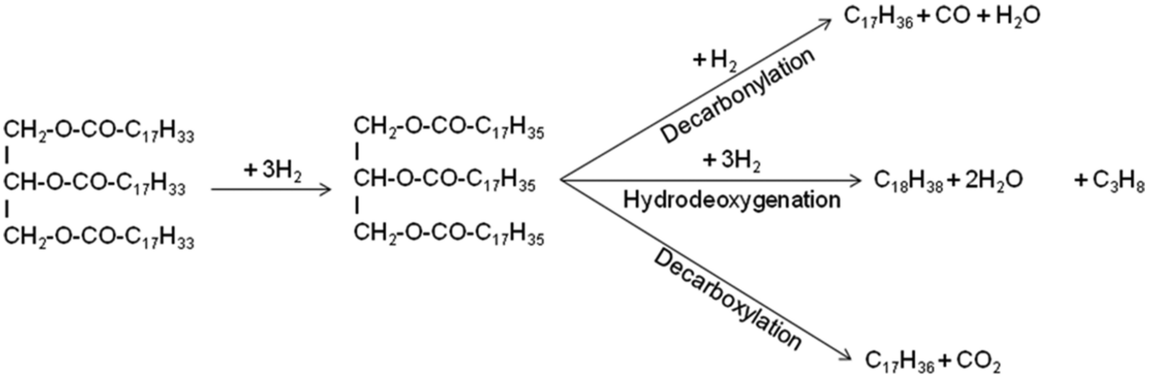


Figure 4.5. Hydrotreatment of triolein.

Both for the fatty acids that for triglycerides, hydrogen is necessary to saturate the double bonds present in the chains. Figure 4.5 shows upgrading of triolein in which each chain has one unsaturation.

4.6 Role of water in the treatment of oils

Hot compressed water is a candidate medium for treatment of fats/oils to produce bio-oil, because of its capability to hydrolyse triglycerides into free fatty acid and glycerol without catalyst [13]. According to what reported in the previous section, to obtain suitable biofuels, decarboxylation of a free fatty acid is a key reaction.

Watanabe [14] showed that the conversion of stearic acid (C18:0) decomposition in argon atmosphere and in absence of water at 400 °C was 50%. The products obtained by the thermal decomposition of stearic acid in argon atmosphere were mainly long chain radical further decomposed into CO or shorter chain carbonyl compound. The major route of reaction was the thermal decomposition and not decarboxylation.

In contrast, in SCW, the carboxyl group was stabilized, and the stearic acid conversion was 2%. The gaseous products were CO and CO_2 and the liquid products were mainly amounts of hydrocarbon (alkane and alkene) and some amounts of carbonyl compounds (aldehydes, ketone and carboxylic acid). The main route of the reaction of stearic acid in SCW was the decarboxylation, but the reaction was very slow [14].

For the catalysed deoxygenation reaction of fatty acid and / or triglyceride, the presence of water enhanced formation of in-situ H_2 that promoted the decarbonylation and the hydrogenation reaction and consequently increased paraffin yields [15, 11]. In addition, water significantly suppressed the side reactions of ketonization and esterification, which occurred in the absence of water [11].

4.7 Properties of water

The role of water is connected to its special properties when it is heated at high temperature [16]. Water at ambient conditions is a polar solvent: this being a good solvent for polar compounds and salts, but it is a weak solvent for non-polar compounds [17]. The liquid water molecules because of interactions between the hydrogen bonds, are organized into small groups called clusters. When the water is heated to high temperature the density decreases as the thermal movement between the molecules increases and the hydrogen bonds become weaker. Consequently, the clusters of water become less stable [18]. Other consequence of the lower density is that the relative static dielectric constant decreases [19]. Therefore, with increasing temperature the solvent polarity decreases. At supercritical conditions ($T > 374°C$ and 22.1 MPa), water behaves as a nonpolar organic solvent with good solubility for organic components and gases and low solubility for salts [19, 20]. But the single water molecules are still polar. In the case that a polar compound or an ion is present in the water, the water molecules in its nearer environment are attracted. In the case of higher multi-valent cations the strong interaction with the oxygen atom leads to an elimination of $H+$ and a strong acidic behaviour.

From the thermodynamic point of view, the reason is that the dissociation of weak acids is endothermic [21]. The water shows self-dissociation i.e. formation of $H+$ and $OH-$ that is influenced by the strong clustering effect [22]. At critical point of the water, the $H+$ and $OH-$ ions can move very fast inside one cluster leading to a high reactivity slightly above the critical temperature, although the total concentration of the two ions (K_w) is lower than in sub-critical hot water [23].

Moreover, the ionic product is higher at subcritical conditions than at ambient ones [19] and water acts as a weak acid and base, becoming stronger because the dissociation is endothermic. Looking at chemical reactions, the rate of acid-catalysed reactions are higher than those assumed as due to the only ionic product, because a hydrogen atom of water comes very near to a reactive centre of an organic molecule inducing a reaction, which at ambient conditions is caused by acids. On the other hand the low density of water above its critical point leads to the break-down of the solvent shell and the ionic product decreases drastically at low densities [24]. In figure 4.6 the variation of the water properties (dielectric constant, ionic product and density) to vary the temperature at constant pressure of 25 MPa.

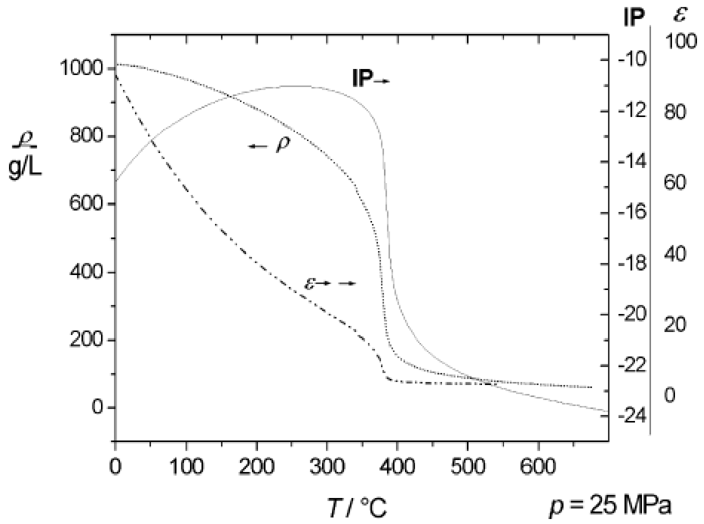


Figure 4.6. Properties of water as function of temperature at 25 MPa (density, dielectric constant and ionic product) [25].

The dielectric constant that affect the water solvent capacity can also affect the energy of activation of the chemical reactions thus varying their rate [26].

Under supercritical conditions the water has properties that are intermediate between a liquid and a gas, with high density than a gas and lower viscosity and higher diffusivity than a liquid.

Hence, the near and supercritical water is a solvent with unique properties, as it can solubilize substances which are not be soluble in water at ambient conditions. Therefore, the heavy compounds like those contained in the tar obtainable by hydrothermal treatment of biomass are more solvated in the reaction medium and better involved in chemical reactions. Some studies show that the amount of heavy carbonaceous products are reduced to a minimum and even absent when the supercritical water conditions are used [27]. Moreover, due to aqueous environment, SCWG can favour the reactions of steam reforming and water gas shift, thus allowing the production of a more hydrogen-rich syngas.

4.8 Thermodynamic and kinetic aspects

For the methane producing reactions noble metal catalysts are required [28, 29], such as Rh, Pd, Pt. In addition, Ni is also indicated as active metal for gasification and selective toward methane formation, for example via the hydrogenation of CO [29].

In Figure 4.7 it is shown the composition of the gas as a function of temperature, assuming a thermodynamic equilibrium for the gasification products of a mixture of glucose (5.4% w/w) and phenol (4.6% w/w) as a model compounds of real biomass [30]. In this mentioned work, the calculations were carried out using Aspen Plus by varying the temperature and considering a pressure of 25 MPa [25].

An important aspect is that thermodynamics provides an almost complete conversion of biomass when the water in the supercritical state is used. Furthermore, in Figure 4.7 it is possible to note that at low temperatures methane formation are favoured, while at higher temperatures the main product is hydrogen [25].

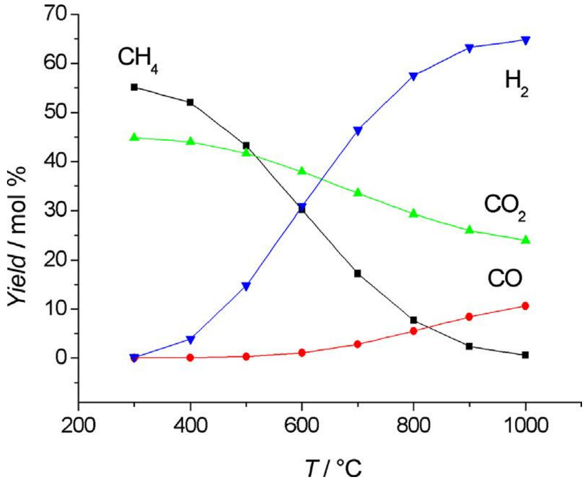


Figure 4.7. The equilibrium gasification yields of a mixture of glucose 5.4% w/w and phenol 4.6% w/w in supercritical water 25MPa [25].

For the model compound (or biomass) lowest concentrations is possible to obtain a higher yield in hydrogen. This can be explained by applying the principles of Le Chatelier to the reactions of hydrogen (1) and methane (2) formation. The reactions for glucose gasification to hydrogen and methane, respectively, can be formally represented as follows:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2 \quad (1)$$

$$C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2 \quad (2)$$

The hydrogen formation requires water, while that of methane not. Therefore, at low concentrations of the feedstock to the equation 1 it is favoured and hydrogen are obtainable in high yields. By increasing the concentration of the material in the reactor, the equation 2 is favoured and methane in high yield increases while hydrogen yield decreases.

In Figure 4.7, it is visible the concentration of CO: this is low at all temperatures. This is caused by the influence of the water gas shift reaction (3).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (3)$$

In this reaction the excess of water displaces the equilibrium (3) towards the formation of hydrogen by reducing the CO yield. In this reaction, we see the role of water that it behaves as a true reagent and contributes to the formation of hydrogen.

In addition to the water gas shift reaction in gas phase reactions take place methanation, which consume hydrogen and CO_x and produce methane. The reactions are shown in (4) and (5).

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad (4)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad (5)$$

The formation of methane from the hydrogenation reaction of CO_x, near the critical point, is kinetically inhibited and requires a catalyst to achieve high yields. Even the water shift reaction is kinetically inhibited.

To obtain high yields of hydrogen, low concentrations of the feedstock in the reactor are preferable and methanation reactions must be hindered. This idea is also at the base of the aqueous phase reforming (APR) process.

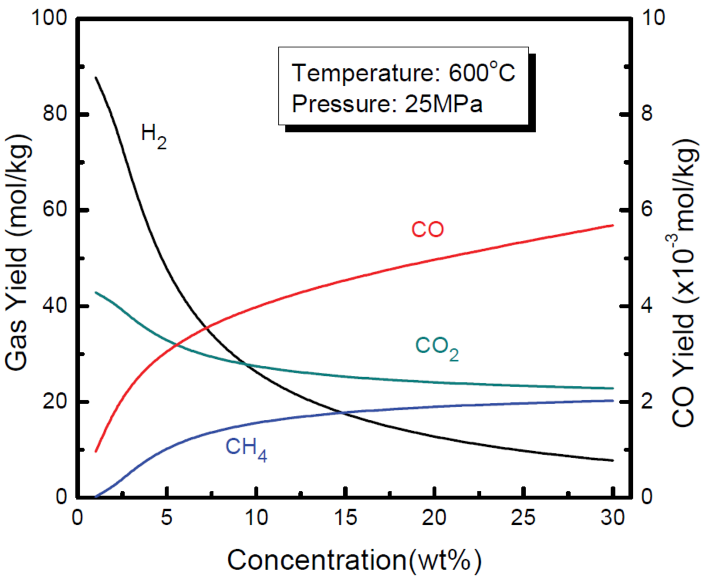


Figure 4.8. Equilibrium gas yields of SCWG of wood sawdust as a function of dry biomass content for biomass gasification at 25 MPa, 600 °C [31].

Figure 4.8 shows the equilibrium composition obtained by the gasification of woody biomass in supercritical water at 600 °C and 25 MPa, varying dry biomass content [31]. It must be noted that the concentration of dry biomass in the reactor must be very low in order to obtain high yields of H_2.

The pressure affects the complicated manner in gasification. The properties of water (density, dielectric constant and ionic product) increases with the pressure. The increase in product ion favors the reactions catalyzed acid, while the radical reactions are disadvantaged.

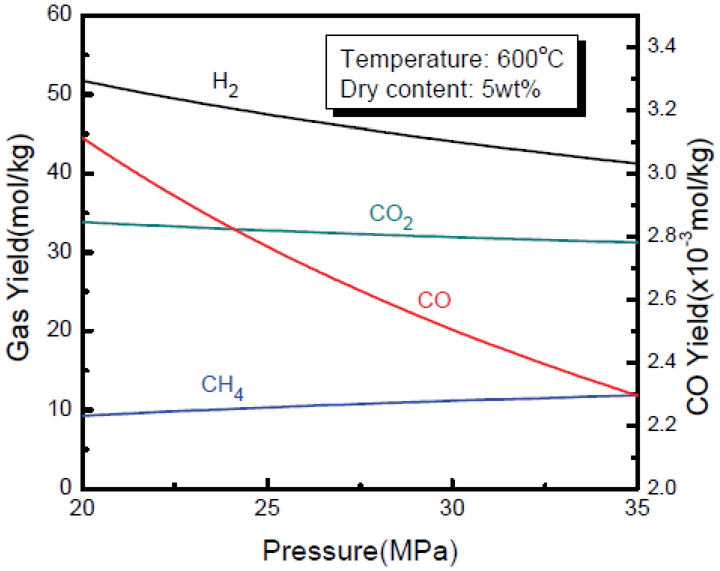


Figure 4.9. Equilibrium gas yields of SCWG of wood sawdust as a function of pressure at 600 °C and dry content 5% w/w [31].

The figure 4.9 shows the effect of pressure on the equilibrium composition for SCWG of woody sawdust to 600 °C and dry biomass 5% w / w. The figure 4.9 shows that the pressure has a weak impact on the equilibrium composition. The concentration of CO decreases because the water gas shift reaction is favored at high pressures [31].

4.9 Upgrading of vegetable oils using heterogeneous catalysts

Heterogeneous catalysts are the most interesting catalytic systems for this type of applications, as they can potentially make the process economically feasible and reduce the environmental impact. Supported catalysts with noble metals, such as Pt, Pd, Ru and cheaper combined transition metals like NiMo, CoMo and NiCo were studied for the hydrodeoxygenation reactions, whereas zeolitic materials were tested as for isomerization reactions due to their structure-acidity properties [32,33]. The homogeneous catalysts are unattractive for these processes, because their use causes problems associated with the environment and increases operating costs.

For biofuels produced from the hydrotreating of vegetable oils, the presence of paraffines without (or very low presence of) sulphur and aromatic compounds is a promising factor required by the fuel selling companies.

Evaluation of heterogeneous catalysts would therefore be very important due to their advantages, with respect to the homogeneous ones, e.g. the easier recovery after the reaction, thus allowing their reuse and avoiding environmental disposal problems [32]. However, a critical issue to be addressed is both thermal and chemical stability, in addition to the good activity and selectivity toward the desired products. The exploitation of homogeneous catalysts could be associated with challenges such as poor thermal stability, difficult and expensive recovery.

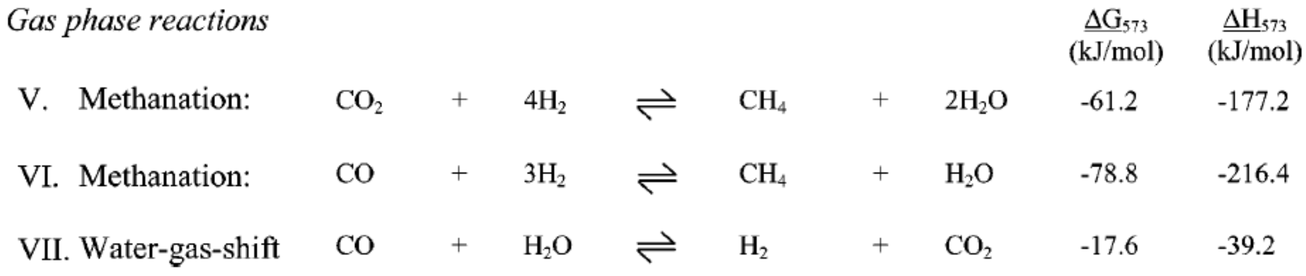
4.10 Reactions with noble metals

Among noble metals, Pd, Ru and Pt are those mainly evaluated for hydrogenation and decarbonylation reactions [34].

A study by Madsen et al. [35] which employed similar loading of Pt or Pd (i.e. 5 wt.%) over Al_2O_3 reported high degree of hydrogenation and decarbonylation with Pt supported catalyst at 325 °C and 20 bar of hydrogen pressure. Oil conversion and alkane yield reached 100%. The higher ratio of odd to even number chains of paraffin indicated the decarbonylation activity to overtake the hydrogenation activity of this catalyst. The authors found that the conversion of the free fatty acids took place faster than that of triglycerides. This was ascribed to the difference in molecular size and diffusivity of the reactants, besides the intrinsic difference in reactivity for esters and carboxylic acids.

Murata et al. [36] performed the processing of jatropha oil with Pt–Re catalyst supported over H-ZSM-5 zeolite at 300 °C and oil to catalyst ratio equal to 1. The characterization of the adopted catalyst showed both Pt and Re to exist as separate active species over the support, although with possibility of synergic interaction.

A study on the reaction pathways and on the effect of the metal loading (39.7-91.9%) of Pd, Pt and Ru supported with Al_2O_3 for the hydro-treating of soybean oil was performed by Veriansyah et al. [37]. The reactions were carried out at 400 °C and 92 bar hydrogen pressure for 2 hours. Paraffin products from the reaction were mainly n-C8 to n-C18 species, with negligible amount (<1%) of n-C19 and n-C20. Hydrodecarboxylation proceeds with the production of n-alkanes with odd number of carbon atoms (n-C15, n-C17, etc.). N-alkane species were also generated through the hydrogenation reaction of free fatty acids of the soybean oil fed together with hydrogen. On the other hand, produced low molecular weight species such as CO and CO_2 interacted with the hydrogen producing methane (methanation V and VI) or with water through the water-gas shift reaction (VII) [12] (figure 4.10).



Gas phase reactions		ΔG_{573} (kJ/mol)	ΔH_{573} (kJ/mol)
V. Methanation:	$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$	-61.2	-177.2
VI. Methanation:	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	-78.8	-216.4
VII. Water-gas-shift	$CO + H_2O \rightleftharpoons H_2 + CO_2$	-17.6	-39.2

Figure 4.10. Thermodynamic data for the methanation and water gas shift reactions, at 300 °C [12].

Catalytic activity of the noble metals followed the order Pd > Pt > Ru [32]. The Pd catalyst produced the highest concentration of n-alkanes (86%) followed by Pt (41%) and Ru (39%). Similarly, the soybean oil conversions were 92, 51 and 40% for Pd, Pt and Ru catalysts, respectively. Species such as cyclic and isomerized alkanes and aromatics, that are associated with good flow properties at low temperature, were not detected with all the materials, suggesting the hydrogenation and decarbonylation as the main reaction pathways. Mohammed et al. [38] and other workers [39–40] have reported a number of reasons which could explain limited performance of the catalysts during the hydrotreatment reactions. Depending on the nature of the support, high reaction temperatures favor catalytic cracking associated with catalyst acidity. The catalyst deactivation was attributed to coke deposition and the presence of impurities in the feedstocks.

4.11 Reactions with other transition metals and effect of catalyst support

Non-noble transition metals refer to pure Ni, Mo, Co, W, their composites (i.e. bimetallic or trimetallic systems) are active catalytic species [32]. These materials, especially the sulphide compounds, have been previously tested in the hydrotreatment of petroleum fractions [42–43], and are therefore currently being evaluated as replacement catalysts for the upgrading of vegetable oils.

The catalyst support represents an important material employed during heterogeneous reactions to enhance the overall activity of the catalyst, by increasing dispersion and accessibility of the reacting species. Supports, which could be oxides, carbon, zeolites, heteropoly acids, etc., are normally solid materials which offer large active surface area for the deposition of active catalyst components. They play vital roles in reactions where the participation of surface catalyst sites is necessary [32]. Supports could either be neutral or containing active sites that also participate in the reaction forming bifunctional (i.e. dual function) catalysts. Therefore, the neutrality, acidity or basicity of a support must carefully be considered before employing it for catalyst design. Historically, transition metals (i.e. pure Ni, Mo, Co, W and their composites) for hydrodecarboxylation reaction are supported on oxides, zeolites or carbon. However, supports with moderate acidity are always preferred because high acidity causes cracking of the generated n-alkanes and therefore reduces their selectivity.

ZSM-5 zeolite has high acidity and showed high cracking rate with difficult to detect amount of desired liquid hydrocarbon products [44]. In the work of Blasco, the SAPO-11 support of moderate acidity showed the highest selectivity (i.e. 100% selective to n-C7–C14 alkanes) [45]. In addition, the increase of Ni loading from 0 to 8% w/w reduces the amount of strong acid sites and allowed production of isomerized alkanes by 85% [32]. The authors [45] reported that to obtain high yield of liquid alkanes in the presence of supports with moderate acidity, the reaction must be carried out at moderate reaction temperatures. Indeed, at higher temperatures, hydrocracking with production of lighter gaseous hydrocarbons (i.e. C1 to C4 compounds) could dominate the reaction. Appropriate loadings of active metal are also very critical for the process [32].

Bimolecular ketonization consists of the union between two carboxyl acids to form a longer symmetric ketone, producing also water and CO_2. The reaction is depicted in Figure 4.11.

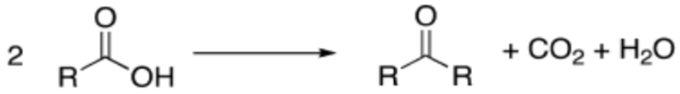


Figure 4.11. Ketonization reaction of two molecules of carboxylic acid [46].

Some authors indicate that the reaction requires a catalyst to take place such as the polycrystalline oxides γ-Al_2O_3, MgO, Fe_3O4, Fe_2O_3, TiO_2, ZrO_2 [46, 47].Therefore these metal oxides often used as supports for catalysts in the processes of deoxygenation of fatty acids could catalyse the ketonization reaction. However, the reaction is not favoured under the operating conditions adopted in these processes and the authors do not consider it.

4.12 Effect of catalyst composition and reaction conditions

Interestingly, NiMo catalyst shows a limited cracking activity, producing mainly C1 to C5 species in trace quantities [48]. Kubicka and Kaluza [49] employed Ni, Mo and NiMo supported with alumina for the upgrading of a food-grade rapeseed oil at variable temperatures (around 300 °C), space velocities (0.25–4.0 h^{-1}) and 35 bar pressure. Under all the tested reaction conditions, supported NiMo catalyst produced the best activity attributed to synergic metallic interactions. For example at 270 °C and 1 h-1, the NiMo catalyst produced almost 100% conversion compared 80% obtained with the Mo and the Ni catalysts. While the selectivity of C5 to C15 alkanes was nearly 100% with NiMo systems, the Ni and Mo catalysts produced respective selectivities of 60 and 50%. Reactions over the Ni/Al_2O_3 involved both hydrogenation and decarboxylation but with the formation of undesired oxygenated intermediates. The Mo/Al_2O_3 on the other hand, produced low yields of alkanes via only the hydrogenation route. The synergic effect in the NiMO/Al_2O_3 catalyst favoured the formation of desired fuel-grade alkanes [50].

In another work, it was found a resulting activity of the tested catalyst according to the following order: NiMo > CoMo > WMo [51]. At 250 °C and 1 h^{-1}, the respective conversions for the NiMo, CoMo and WMo catalysts were 100, 80 and 60%. Similarly, the corresponding selectivity to liquid alkanes were 98, 70 and 50%, respectively. Synergic interaction between Ni and Mo was more pronounced than in other metal combinations. The authors also found the synergism to be support dependent. Catalysts supported over SiO_2 were more active producing from 80 to almost 100% conversion than those supported over Al_2O_3 or TiO_2 that produced less than 80% conversions under comparable reaction conditions [50].

Trimetallic systems (i.e. to form NiCoMo catalyst) demonstrated improved performance in all cases. The reaction products composed mainly of alkanes (both n- and i-) with >85% selectivity and limited side reactions. These types of catalysts should further be evaluated to fully establish their modes of action, the extent of inter-metallic synergic interaction and how the addition of a third metal modifies the catalyst textural surface [32].

4.13 Hydroisomerization of the hydrocarbons products

The normal paraffinic hydrocarbons produced from hydrotreatment of vegetable oils are associated with non-compatible cold flow characteristics. They can therefore be blended only in low ratios with jet fuels. To appropriately improve these properties, the n-paraffins must be converted/upgraded into the corresponding iso-paraffins by hydroisomerization process (Fig. 4.12) [32].

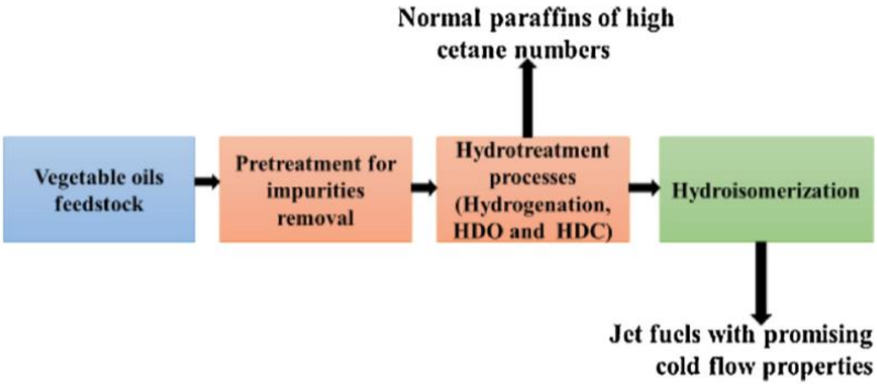


Figure 4.12. Block diagram for hydrotreatment and hydroisomerization of vegetable oil [32].

However, when the chain length of the n-alkane produced from hydrotreatment reaction exceeds n-C15, a further hydrocracking to lighter alkanes is necessary before the hydroisomerization reaction [32]. The hydrocracking of alkanes is a known industrial process already developed by the petroleum refineries for the production of gaseous hydrocarbons, gasoline, kerosene, etc. from heavy fractions.

4.14 Production and consumption of hydrogen for hydrogenation of oils

A key issue for fatty acid deoxygenation is that the process requires additional H_2 [52]. For example, one mole of H_2 to decarbonylate one mole of fatty acid. In addition, hydrogen also serves to saturate the double bonds possibly present in the fatty acid chains. As already above, consumption of hydrogen may occurs also in the gaseous phase due to effect of methanation reactions.

Indeed, without an external H_2 supply, nickel-based catalysts showed low activity toward fatty acid deoxygenation (20% conversion rate) [52].

Santillan- Jimenez et al. studied stearic acid deoxygenation over Ni/C catalyst using different concentrations of H_2 [52]. Only 19% of stearic acid conversion was achieved without adding H_2, while 64% and 80% conversion were obtained under, respectively, 10 and 100% vol/vol of H_2 in the initial atmosphere, at 300 °C, 135 psi and for a reaction time of 1.5 h. However, it would be important to develop a process to improve the fatty acid conversion to hydrocarbons under no or low external addition of H_2.

Vardon et al. investigated the possible in-situ generation of hydrogen on catalytic deoxygenation of fatty acids in hydrothermal process, which used water as solvent. In particular, glycerol was added to generate H_2 via aqueous phase reforming reaction. Although this process successfully reduced the consumption of H_2, the cost of glycerol also needs to be considered [53].

Some studies have tried to explore the potential of the hydrothermal process to in-situ generate H_2 directly from fatty acids and subsequently use it to promote FAs decarbonylation [11]. The in-situ H_2 could be formed through the feedstock reforming and the water–gas shift reactions [50]. In a hydrothermal environment, CO is expected to be released via decarbonylation, and to react with H_2O to produce in-situ H_2 [11]. Aqueous phase reforming of organic acids has also been reported over Ni based catalysts, generating CO_2 and H_2 as the main products [54]. In principle, under hydrothermal conditions aqueous phase reforming and water–gas shift could produce the required H_2 for fatty acid deoxygenation.

Some studies attempt to fill an important information gap on the use of the in-situ, self-generated H_2 to deoxygenate fatty acids. They investigated the performance of fatty acid hydrothermal catalytic deoxygenation, using palmitic acid (PA) as a model compound and Ni/ZrO_2 as a catalyst [11]. They demonstrates that hydrothermal process at 300 °C and 100 psi H_2 pressure, over a 10% w/w Ni/ZrO_2 catalyst, 88.2% of the carbon initially contained in the PA was converted and gave a paraffin yield of 60.7%. With the same process, but in the absence of externally added H_2, PA carbon conversion reached 64.2% of and paraffin yield reached 38.6%; both this values were much higher than the results achieved in the absence of water [11]. Decarbonylation was found to be the major route for producing paraffin in hydrothermal catalytic deoxygenation in the presence of a Ni/ZrO_2 catalyst. The presence of water enhanced formation of in-situ H_2 that promoted PA decarbonylation and increased paraffin yields. In addition, water significantly suppressed the side reactions of ketonization and esterification [11].

4.15 Hydrogen production from glycerol

The utilization biodiesel co-products, like the glycerol obtained with the transesterification of vegetable oils, is one of the main options to be considered to lower the overall cost of the biodiesel production [2, 55]. In recent years, many studies have focused in the valorization of high quality glycerol by-product.

For example, the glycerol may represent a potential source for hydrogen production. Glycerol can be efficiently converted in hydrogen by means of its catalytic steam reforming according to the following reaction:

$$C_3H_8O_3 + 3H_2O \longrightarrow 3CO_2 + 7H_2$$

The steam reforming (SR) of hydrocarbons is a catalytic process that typically takes place in vapour phase at atmospheric pressure and temperatures around 1073 K.

Nevertheless it has been reported [2] the possibility to obtain hydrogen from oxygenated hydrocarbons having a C:O stoichiometry of 1:1 and at low temperature (500 K) and high pressure (2–5 MPa) by aqueous-phase reforming (APR) process. Catalysts for steam reforming of hydrocarbons are mainly based on nickel as active component supported on oxides with high thermal stability, such as TiO_2, ZrO_2 and Al_2O_3 [56]. Although noble metals (Ru, Rh, Pt and Pd) are more effective for the steam reforming of hydrocarbons than Ni and less susceptible to coke formation, they are not commonly used as catalysts in industrial applications because of their high cost [56]. In general, an effective catalyst for the production of hydrogen by aqueous phase reforming of oxygenated hydrocarbons should break C–C, O–H and C–H bonds in the oxygenated hydrocarbon reactant and facilitate the water–gas shift reaction to remove the adsorbed CO from the catalyst surface. Studies on aqueous phase reforming of oxygenated hydrocarbons over various supported metals [57, 58] indicate that Pt (more) and Pd catalysts are, active and selective for the production of hydrogen. Nevertheless, the high cost and limited availability of noble metals make it of particular interest to develop less expensive catalyst for aqueous phase reforming.

From the above reasons, in the present work nickel was selected as active metal to be included in catalyst formulations applied to glycerol reforming.

The structural characteristics and performance of supported nickel catalysts are strongly influenced by the nature of support on which the metallic crystallites are deposited. The use of supports with high thermal stability that stabilizes nickel particles against sintering and that promotes the carbon gasification are necessary to develop suitable catalysts for the steam reforming of glycerol.

To provide these operational advantages different promoters are usually included in the reforming catalyst formulations. Magnesium is widely used as promoter in Ni/Al_2O_3 catalysts applied to steam reforming of hydrocarbons since it enhances both the steam adsorption capability and the stability of nickel against sintering [59]. The addition of ZrO_2 to reforming catalysts is also claimed in literature [60] as an element able to improve the stability of nickel catalysts in the steam reforming of hydrocarbons.

4.16 Experimental setup

Five reactors made of SS316 steel were used to conduct the experiments. The pressure and the maximum temperature indicated is 200 bar and 450 °C respectively, the volume of each reactor is 24.5 ml.

The typical reactor was home-made in KIT in all its parts. The apparatus for purging the reaction volume and for the collection of gas products is shown below (figure 4.13). The system consists of a metallic cylindrical chamber (bomb) where one can enter the reactor and open or close it avoiding that gases are dispersed.

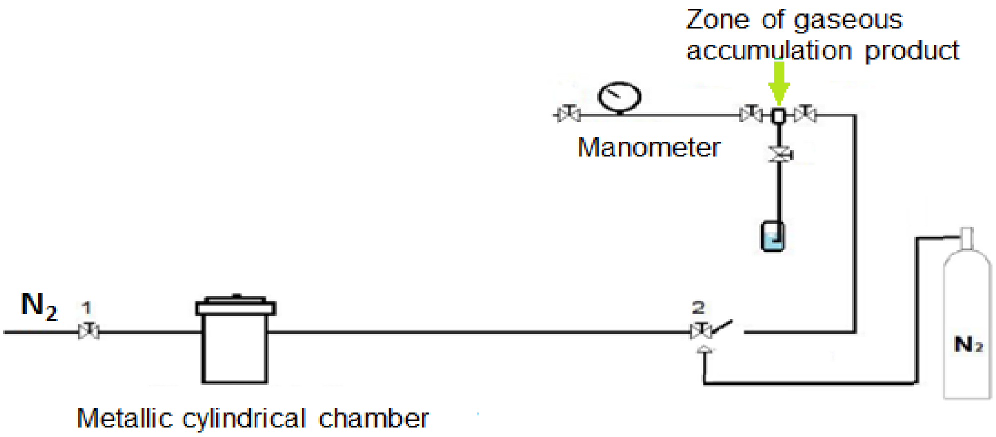


Figure 4.13. Representation of the system of collection of the gas phase.

During the purging procedure the bomb is connected to a nitrogen cylinder (valve 2, see figure 4.13), while in the gas collection procedure (after the reaction) the bomb is connected to a line equipped with a precision pressure gauge and a septum for drawing gas samples by a syringe.

The reagent, the water and the catalyst are loaded in appropriate amounts and the reaction medium is purged with nitrogen to expel the oxygen inside the reactor. The purging procedure provides for: the introduction of nitrogen at a pressure of about 5 bar (valve 1 close and valve 2 open, see figure 4.13), the insulation of the volume of the bomb, closing valve 2, at the end the gas expulsion opening valve 1. The procedure is repeated 5 or 6 times.

During the sampling of the gaseous phase, the bomb is connected to the line in which is present the pressure gauge and the septum for gas sampling. The reactor is placed inside the bomb, but before opening a stream of nitrogen is sent (by the valve 1) to eliminate the oxygen present in the internal volume of the apparatus. After this operation, the valves are closed, and the operator proceeds with the opening of the reactor. The gas that comes out can expand within the volume of the system and causes a pressure increase that is measured by the pressure gauge. At this point gas sample is taken from the septum, using a GC syringe.

4.17 Materials and methods

The materials used for the experiments as reagents are: rapeseed oil for food purchased at the supermarket, stearic acid (> 97%) and glycerol (> 98%) purchased from the Merck. The materials used as catalysts are: Raney nickel by Merck, zirconia oxide (IV), (> 99%) from Alfa Aesar, zirconium hydroxide (IV) (> 97%) from Sigma-Aldrich. Other nickel based catalysts supported on metal oxides of different nature were prepared in the laboratory of department of catalysis in KIT for a different project.

The following alkanes were used as standards for calibration of the GC: n-decane, n-dodecane, n-tridecane, n-pentadecane, n-heptadecane and n-octadecane. For other alkanes of different length the same response factors of the standard available were used.

The zirconium hydroxide was calcined at 400 °C in air for three hours to obtain zirconia (ZrO_2).

A typical experiment involves the use of 250 mg of stearic acid, 4.75 g of deionized water and 35 mg of Raney nickel catalyst, or 250 mg for the other catalysts.

For the experiments with the glycerol, an aqueous solution of glycerol at a concentration of 2.5% by weight (0.29 M) was used and 35 mg of Raney nickel or 250 mg of other catalysts were added.

The identification and quantification of the gaseous products were accomplished by GC Agilent 7890A model with two column: Glass Packed Column GC 80/100 Porapak Q support, L × O.D. × i.d. 6.0 ft (1.8 m) x 1/4 in. × 2.0 mm - FID detector, MOLESIEVE 5A 80/100 6FT, 1/8 IN SS - TCD detector.

For the analysis of liquid samples an Agilent 7890B GC - FID equipped with Restek Stabilwax-DA 30 m x 250 mm x 0.25μm capillary column was used.

For identification of liquid products a GC-MS equipped with Agilent 6890N Rxi-5Sil MS capillary column 30m, 0.25mm, 0.25μm was used.

The aqueous phase was analysed with liquid chromatography HPLC Hitachi Model Primaide, equipped with Aminex HPX 87H column.

4.17.1 Physical conditions and pressure

Under operating conditions below the critical point the water pressure is dictated by the liquid-vapour equilibria of water while at temperature higher than the critical it depends on the density. In supercritical water there is only one phase whose density is calculated as the ratio between the mass of water and the volume available in the reactor. With this input data the pressure was predicted using the Span Wagner EOS.

In subcritical condition liquid and vapour phase coexist. In this case the pressure was calculated with the Antoine equation. The densities were calculated the same EOS mentioned earlier. The table 4.1 summarize the physical conditions of water in the reactor in subcritical and supercritical state.

Physical conditions	**T [°C]**	**P [bar]**	**Number of phases**	**ρliq [g/ml]**	**ρgas [g/ml]**	**Method of calculating**
Supercritical water (SCW)	375	221	1	ρliq=ρgas=0,210 g/ml (mass H_2O/volume reactor)		S&W EOS
Subcritical water	350	163	2	0,575	0,114	Antoine equation and S&W EOS

Table 4.1. Physical conditions of water in the reactor in subcritical and supercritical state.

4.17.2 Heating procedure

For the heating of the reactors, a GC oven was used. The temperature program changes with the desired reaction temperatures, but consists of the same steps. It firstly has a phase (x1) where the oven temperature is set to 400 °C (maximum temperature reachable by the device). Once this period is completed, the oven temperature is set at 20 °C for a predetermined time (x2). During this step, the temperature of the oven decreases, while the temperature inside the autoclave is still rising. At the end of these two steps, the reactor has reached the desired reaction temperature.

The time values adopted for each step are shown in table 4.2.

Desired reaction temperature [°C]	x1[min]	x2[min]	Total (x1+x2) [min]
300	14:35	0:38	15:13
325	16:21	0:28	16:49
350	18:07	0:19	18:26
375	19:35	0:10	19:45

Table 4.2: Values of x1 and x2 for each reaction temperature

The times x1 and x2 are calculated using the following equations:

$$x_1 = \frac{T - 268.7\,°C}{0.258\,\frac{°C}{sec}} - \frac{402.4\,°C - T}{2.727\,\frac{°C}{sec}}$$

$$x_2 = \frac{402.4\,°C - T}{2.727\,\frac{°C}{sec}}$$

With T equal to the desired temperature for the reaction. The thermal profile in the system is represented in figure 4.14 which shows the furnace temperature (orange line) and the inner profile to the reactor (green line) for an experiment at 350 °C.

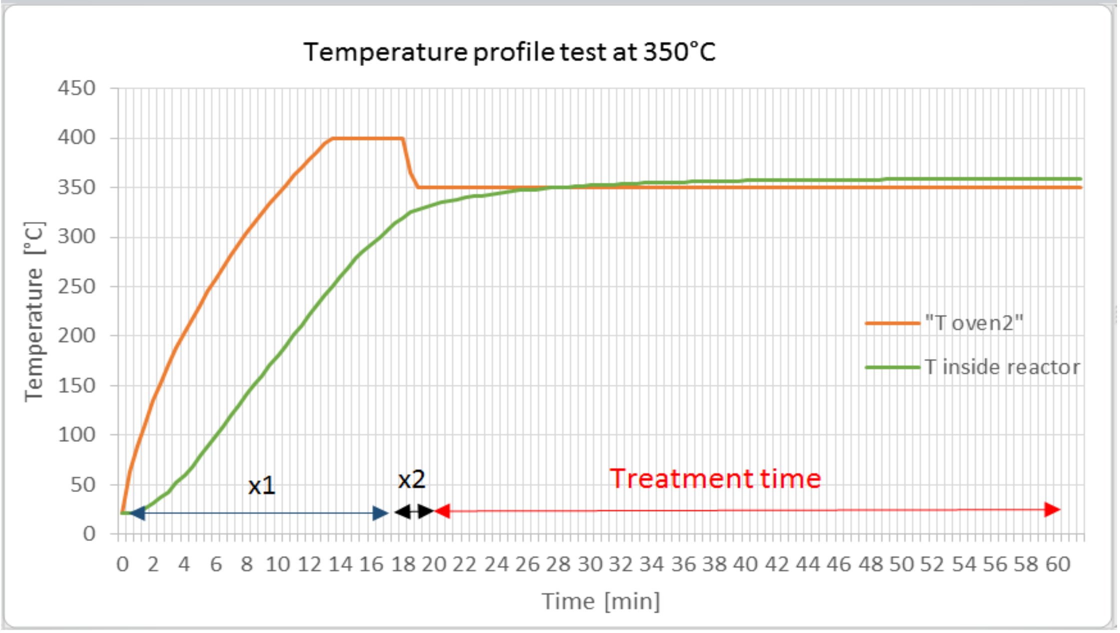


Figure 4.14. Thermal profile in the system.

At the end of the reaction time, the oven is opened and the reactor is cooled in ice and water. The rapid cooling has the purpose of arresting the chemical reactions.

4.17.3 Sample preparation and analysis

Gas samples were taken from the collection system with GC syringes of 100 and 500 microliters and directly injected into the chromatographic analysers.

To identify the products in the liquid phase by GC-MS, the sample must be water free since the column it is not compatible with this molecule. Then, the sample is mixed with dichloromethane

(DCM) in order to obtain two distinct phases: the aqueous phase is removed, and the organic phase, in which all the products of the reaction are solubilized, is analysed by GC-MS.

The GC-FID used for the quantitative analysis is equipped with a column capable of processing samples with high water content as solvent medium. For this reason, the samples were solubilized in tetrahydrofuran (THF) which has the ability to mix with the water sample and solubilize the apolar compound. With the addition of THF a single homogeneous phase was obtained and the sample directly analysed.

For the tests conducted on glycerol, the aqueous phase was withdrawn and directly analysed by liquid chromatography without the addition of other solvents.

All the liquid products were filtered by 0.45 µm membrane filter before being analysed.

4.17.4 Conversion parameters

Mass efficiency parameters for the deoxygenation of stearic acid (SA) to alkanes were calculated. The calculation is based on the assumption that each molecule of produced alkane whose chain length is comprised between ten and eighteen carbon atoms (C10 - C18) is obtained by deoxygenation and fragmentation of a molecule of stearic acid (C18 acid). Liquid hydrocarbons, shorter than C10 are not visible to the GC because the used method of analysis does not allow to measure them. The conversion was calculated as ratio between the reacted moles of SA and the loaded moles of SA. The yield of alkanes was calculated as the ratio between the sum of the moles of obtained alkanes (measurable) and the initial moles of SA. The selectivity to the target product (heptadecane or C17) was calculated as the ratio between the moles of C17 and the initial moles of SA. The following are the formulas used to calculate the performance parameters in the liquid phase.

$$\boldsymbol{Conversion} = 1 - \frac{Final\ mol\ SA}{Initial\ mol\ SA};$$

$$\boldsymbol{Yield} = \frac{\sum Mol\ of\ paraffins\ (C10 - C17) in\ the\ product}{Initial\ mol\ of\ SA};$$

$$\boldsymbol{Selectivity\ of\ heptadecane} = \frac{Mol\ of\ C17}{Initial\ mol\ of\ SA}$$

Another possibility to calculate the conversion parameters is the balance of carbon atoms. Because of water is involved in some reactions (i.e. water gas shift) the mass balance between products and reagents could give product mass yield higher than 100%.

For the gas phase, the carbon gasification ratio parameter (CGR%) hydrogen gasification ratio (HGR%) and oxygen gasification ratio (OGR%) were calculated. The maximum limit of CGR is 100% while the other two parameters can be greater than 100% given that hydrogen and oxygen can originate from the water for a complete gasification.

$$\boldsymbol{CGR}\% = \frac{Mol\ Carbon\ gas}{Mol\ Carbon\ feed}; \qquad \boldsymbol{HGR}\% = \frac{Mol\ Hydrogen\ gas}{Mol\ Hydrogen\ feed}; \qquad \boldsymbol{OGR}\% = \frac{Mol\ Oxygen\ gas}{Mol\ Oxygen\ feed}$$

For the experiments with glycerol, instead, the liquid phase is analysed by HPLC and the results are expressed as mass concentration of the individual components in the liquid phase, with respect to the initial mass of glycerol.

4.18 Test with stearic acid

The gasification indexes were calculated for the test without catalyst and in the presence of zirconia after two hours of reaction time. The CGR%, HGR% and OGR% values were all lower than 0.43% indicating that stearic acid does not react to give gaseous products in significant amounts in water in the absence of catalyst at 375 °C even after 120 minutes. Also in the presence of ZrO_2 no significant amounts of gas was obtained, which suggests that this oxide has no catalytic effect for the reaction of interest.

The same gasification indexes were calculated for the experiments conducted in the presence of Raney nickel catalyst. In figure 4.15 these parameters are reported for experiments of 60 minutes, at 375 °C, 350 °C and 325 °C.

In the presence of Raney nickel the amount of gas is very high, in fact up to 47.5% of the carbon present in the reagent at the end of the reaction is incorporated in the gaseous products (mainly CO_2, CH_4, and in minimal amounts, C2, C3 and C4 hydrocarbons). The OGR value reaches 270%: this means that oxygen initially present in SA has been transferred to gas products together with O coming from water.

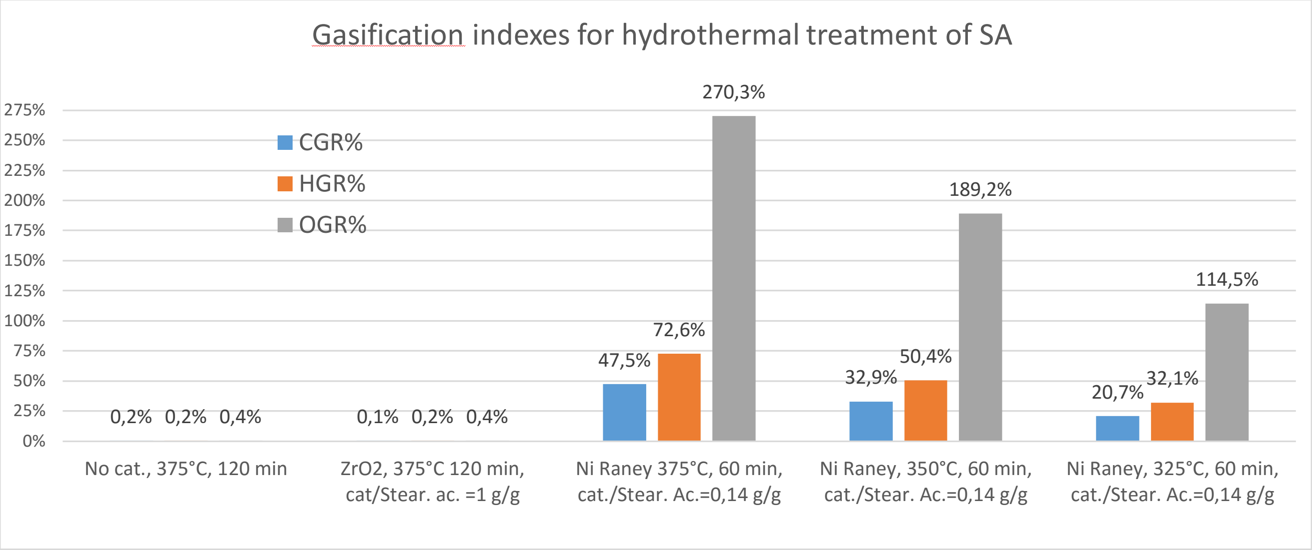


Figure 4.15. Gasification indexes (CGR%, HGR%, OGR%) for hydrothermal treatment of stearic acid (SA/water 5% w/w) with different catalyst and various operative conditions.

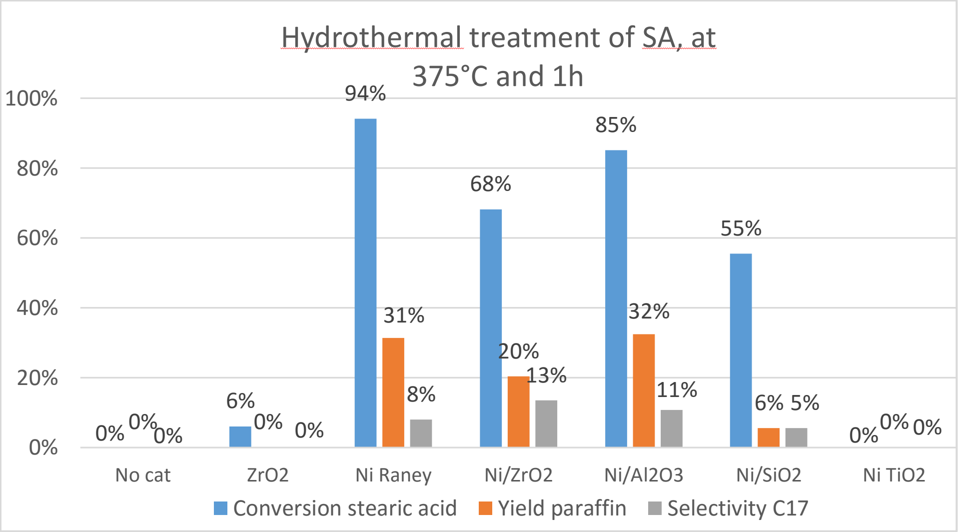
The HGR index reached a maximum of 72.6% after one hour of treatment, which is a cumulative value between the hydrogen coming from the reforming of the fatty acid, and hydrogen produced by water splitting.

The values of the indexes vary considerably with temperature: at higher temperature, parameters are high; decreasing the temperature instead, the values seem to decrease linearly.

4.18.1 Analysis of liquid products

A comparison among the results of tests conducted on stearic acid at 375 °C with one hour of reaction time and various catalysts is shown in Figure 4.16. The catalysts based on nickel supported on oxides were prepared in IKFT department (see paragraph 4.1). The table shows the concentration of nickel in catalysts and the mass ratio between catalyst and stearic acid.

In the absence of catalyst it was verified that the stearic acid does not undergo transformations. In the presence of zirconia (ZrO_2) with catalyst / stearic acid mass ratio equal to 1, the conversion was low (5.9%) and no trace of paraffin was found.



Catalyst	Nickel Loading (wt%)
Ni Raney	>90,0%
Ni/ZrO$_2$	5,8 %
Ni/Al$_2$O$_3$	20,0 %
Ni/SiO$_2$	22,0%
Ni/TiO$_2$	5,8 %

Figure 4.16. Hydrothermal treatment of stearic acid (SA/water 5% w/w) using different heterogeneous catalysts at 375 °C and 1 hour.

Nickel showed good activity in these operating conditions. In particular, the tests with Raney nickel, with a catalyst / stearic acid ratio equal to 0.14 was able to convert almost all the reagent present in the reactor (94.2%). All other experiments were done with catalyst / reagent mass ratio equal to 1. The nickel-based catalysts supported on zirconium oxide, alumina and silicon made possible to convert a substantial amount of SA in paraffins, while Ni supported on titanium oxide was inactive. The nickel-based catalysts supported on ZrO$_2$ and Al$_2$O$_3$ have given the highest selectivity in heptadecane (13.4% and 10.8% respectively). Despite the concentration of nickel is equal to the catalysts Ni/ZrO$_2$ and Ni/TiO$_2$ performance catalysts are very different. In particular, Ni/TiO$_2$ showed no catalytic activity. This result suggests that the support can influence the performance of the catalyst. The catalyst supported on SiO$_2$ proved to be less active than the catalyst with Al$_2$O$_3$ support despite the amount of nickel is very similar. Even in this case by comparing test results with similar catalyst concentration but different catalytic supports, different results were obtained. These results show that the choice of the support may have a crucial importance for the performance of the catalyst on the deoxygenation of stearic acid.

4.18.2 Effect of treatment time and temperature

Experiments in supercritical water (375 °C) in the presence of Raney nickel and a catalyst / stearic acid 0.14 g / g ratio were performed at different times of treatment and compared (see Figure 4.17). For very short reaction time (15 minutes) 27% of stearic acid, initially present was converted into other products. After half an hour of treatment, the conversion reached a value of 84%, while after

45 minutes the conversion was virtually complete. The yield of alkanes increased with the test time up to a maximum after 45 min (43%) and then decreased to 31% when reaction time increased to an hour.

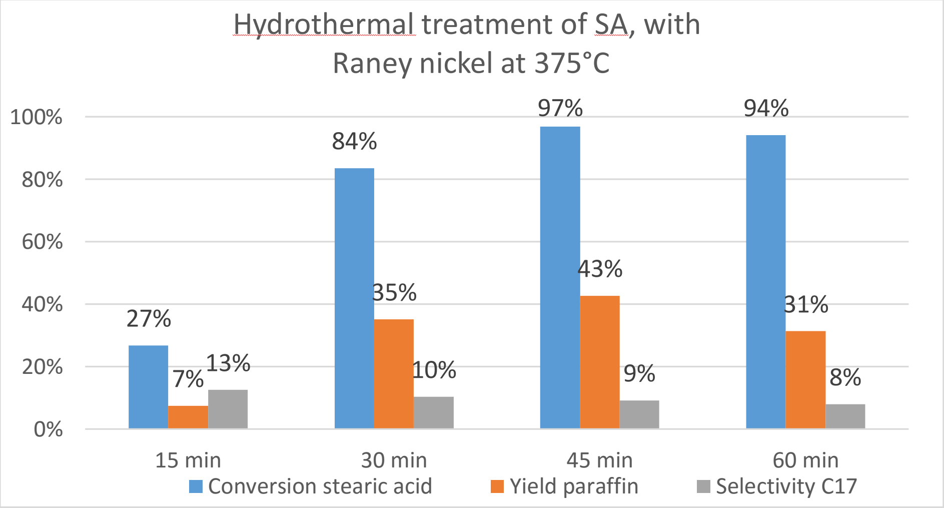


Figure 4.17. Hydrothermal treatment of stearic acid (SA/water 5% w/w) in the presence of Raney nickel (mass ratio Raney nickel/SA =0.14 g/g) at 375 °C and different reaction time.

The selectivity in heptadecane is low for all experiments in the supercritical condition and appears to decrease for high treatment times.

The same trend was obtained in subcritical water (350 °C, see figure 4.18), in fact, conversion increased from 30 to 66% by increasing the treatment time, the yield of alkane and selectivity in heptadecane, however, seem to increase for relatively short treatment times (30 - 60 minutes), and decrease for very high treatment times (120 minutes).

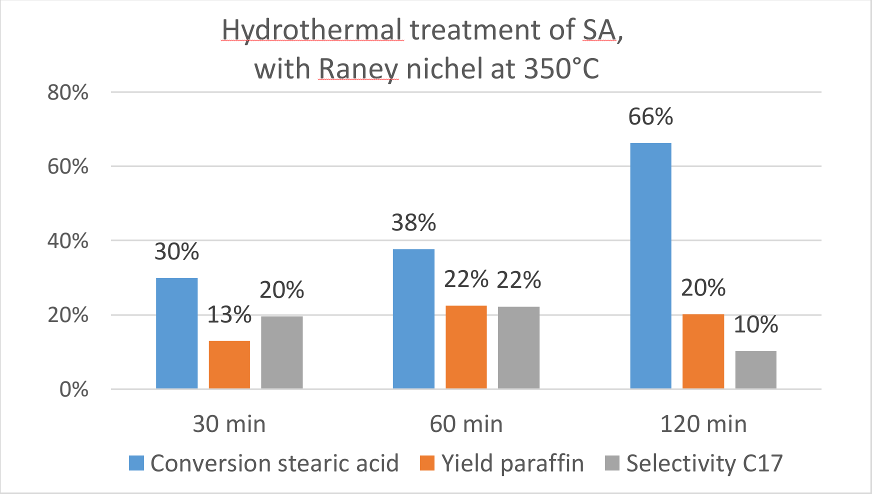


Figure 4.18. Hydrothermal treatment of stearic acid (SA/water 5% w/w) in the presence of Raney nickel (mass ratio Raney nickel/SA =0.14 g/g) at 350 °C and different reaction time.

To study the effect of temperature on the performances of the process a test was also done at a lower temperature of 325 °C, (Figure 4.19). At fixed operating conditions, when the temperature decreased the reaction kinetics was slowed down, in fact lower conversions and yields paraffin were obtained in.

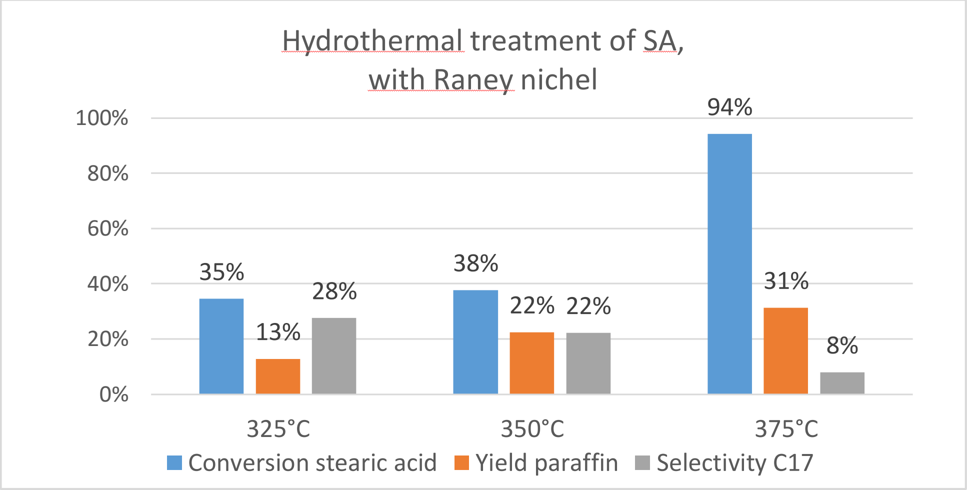


Figure 4.19. Hydrothermal treatment of stearic acid (SA/water 5% w/w) in the presence of Raney nickel (mass ratio Raney nickel/SA =0.14 g/g) at different temperature and reaction time 1 hour.

For what concern the selectivity we observed that it increased by decreasing the severity of the process. Anyway, such higher selectivity values were not effective in improving the paraffin yields. These results suggest that the temperature is a very important parameter for this process and that the optimal conditions must be sought in order to obtain good yields in relatively short times.

4.18.3 Effect of H_2 pressure and catalyst concentration

The test at 375 °C and with one hour of treatment time was also carried out in the presence of an external hydrogen pressure. The purging of the reactor volume was made with hydrogen instead of nitrogen and a pressure of 5 bar of hydrogen was loaded (see Figure 4.20). As expected, for this experiment both the yield of paraffin and the selectivity in heptadecane increased compared to test an inert environment.

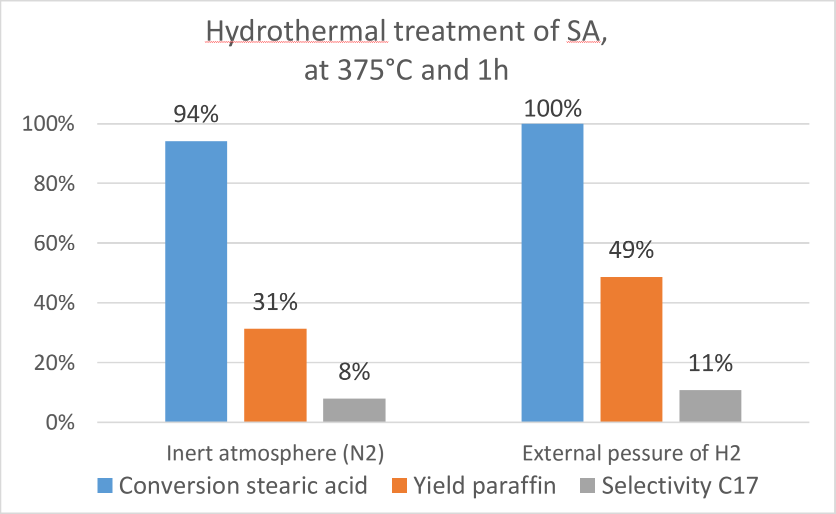


Figure 4.20. Hydrothermal treatment of stearic acid (SA/water 5% w/w) in the presence of Raney nickel (mass ratio Raney nickel/SA =0.14 g/g), reaction time 1 hour in inert atmosphere and under 5 bar H_2 external pressure.

In Figure 4.21 two tests performed under the same operating conditions but with different concentration of catalyst are compared. Higher yield and selectivity were obtained when the concentration of catalyst was reduced by 50%, while the conversion remained very similar for both tests.

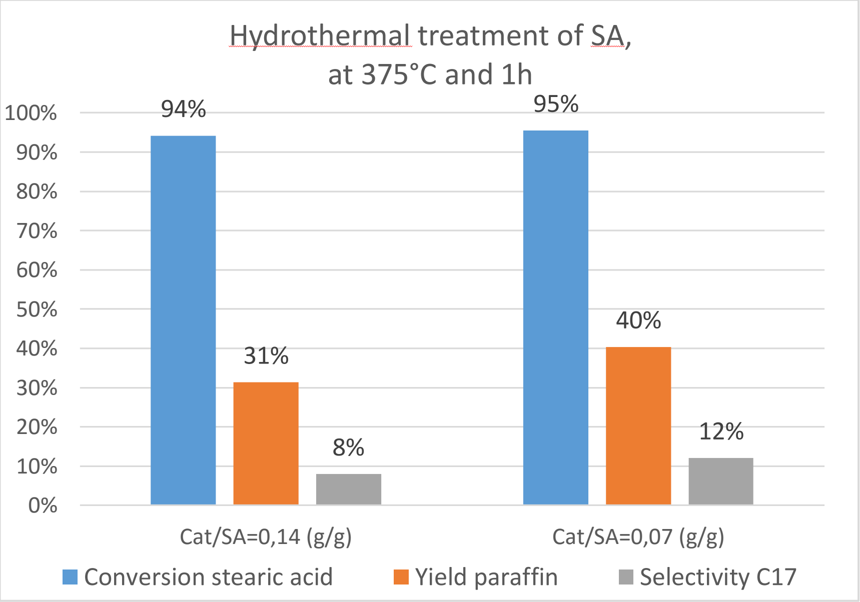


Figure 4.21. Hydrothermal treatment of stearic acid (SA/water 5% w/w) in the presence of Raney nickel at 375°C, reaction time 1 hour varying the catalyst concentration.

This result can be explained by assuming that the excess of catalyst with respect to 0.07 g/g concentration promotes the gasification of the feed at adopted operating conditions. Raney nickel catalyst being active also for the gasification must be used at lower concentrations to avoid the decomposition of hydrocarbons. Another strategy would be to use a treatment time which avoids the gasification of hydrocarbons obtained. The results obtained by varying the treatment time (figure 4.17 and 4.18) also suggest that a too high time decreases the yield of paraffins. The use of a continuous plant for these processes make it possible to use the optimal reaction conditions and consequently maximize the production of alkanes.

4.18.4 Gas phase composition

From the hydrothermal conversion of stearic acid, a high amount of low molecular weight components is obtained. Hydrogen, carbon dioxide and methane are the main components, while ethylene, ethane, propylene, propane and carbon monoxide are always present in amount lower than one percent of the volume of the gas. The butane component is hardly detectable by the GC analysis.

Figure 4.22 illustrates a typical analysis of the gas phase obtained in a test at 375 °C and 60 minutes of treatment time. Also for the other tests conducted at different operating conditions the composition of the gas phase was very similar. Methane is always present in a range between 47 and 55% vol / vol, followed by carbon dioxide present between 26 and 29% and hydrogen ranging between 17 and 22%. All other gaseous components account for less than 1.5% vol/vol.

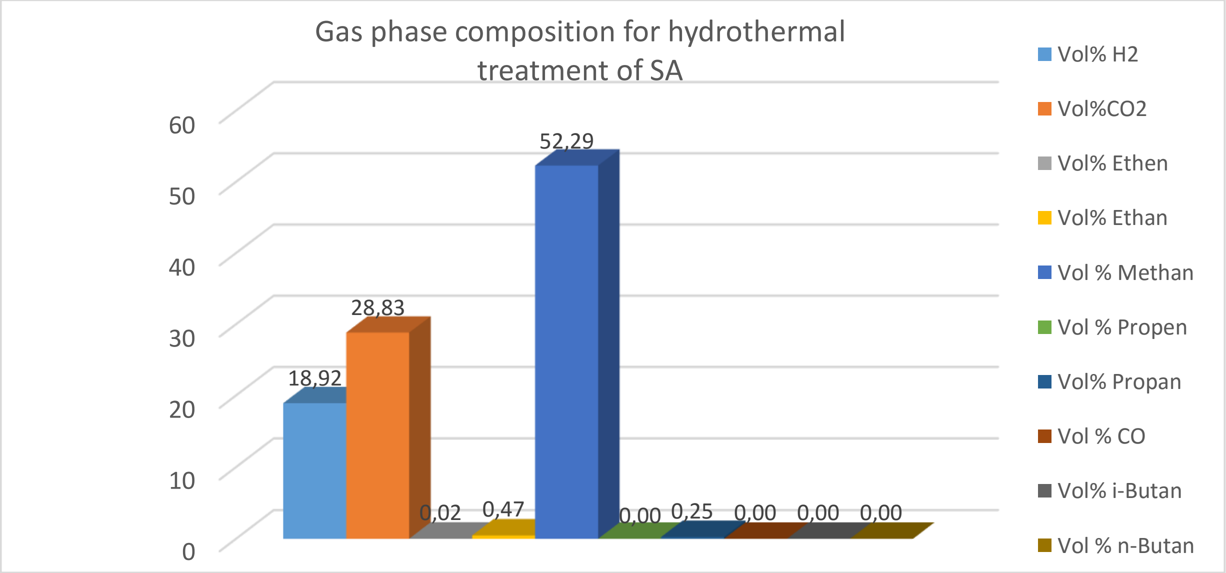


Figure 4.22. Gas phase composition obtained from hydrothermal treatment of stearic acid (SA/water 5% w/w) in the presence of Raney nickel (mass ratio Raney nickel/SA =0.14 g/g) at 375°C, reaction time 1 hour.

4.18.5 Atomic carbon balance

According to the results of the analysis of the liquid and gas phases an atomic balance on carbon was performed.

The results are reported in Figure 4.23 and one can observe that the sum of the fractions of carbon atoms in the liquid and in the gas phase is very close to 100%. This result suggests that the amount of not detectable alkanes (i.e. alkanes consisting of a number of carbons between C5 and C9) are formed in too low amount to affect the obtained balance.

The value of carbon balance close to 100% also suggest that the carbon is substantially distributed in the gas and liquid phases, and that negligible amount of solid phase are generated.

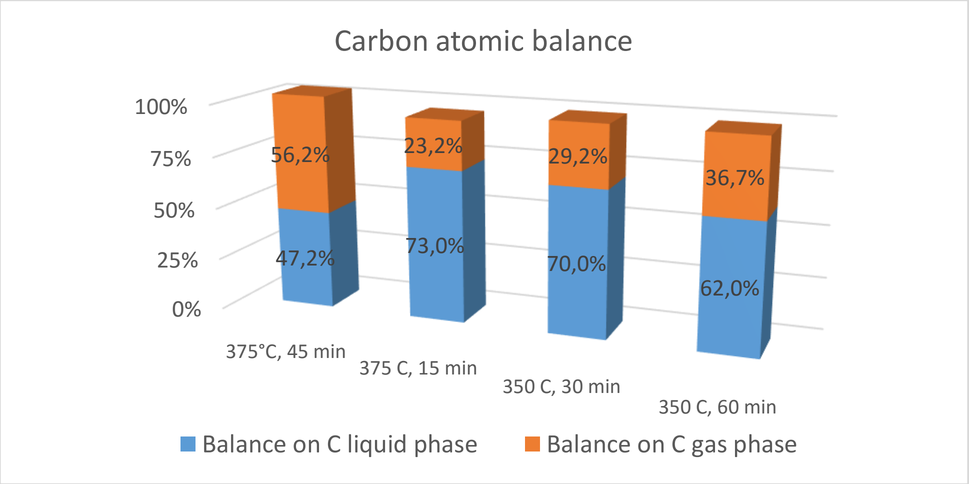


Figure 4.23. Carbon atomic balance obtained for hydrothermal treatment of stearic acid (SA/water 5% w/w) in the presence of Raney nickel (mass ratio Raney nickel/SA =0.14 g/g) at different operating conditions.

4.19 Test with glycerol

As explained in the early part of the chapter, glycerol is inevitably produced by the hydrolysis of triglycerides and considered a co-produced. One way to exploit the glycerol may be the gasification for the production of hydrogen to be used for the hydrodeoxygenation of fatty acids. In this manner, one may decrease or cancel the request of hydrogen from other sources, making the process self-sustainable and economically viable.

Some experiments were performed with glycerol to study the possibility of using this molecule as a source of hydrogen. Tests were done using an aqueous solution at 2.5% w / w in glycerol (adopted volume of 4.75 ml).

Tests were done without catalyst, with zirconia oxide (ZrO_2) and Raney nickel and the obtained gasification parameters (CGR%, HGR% and OGR%) were compared.

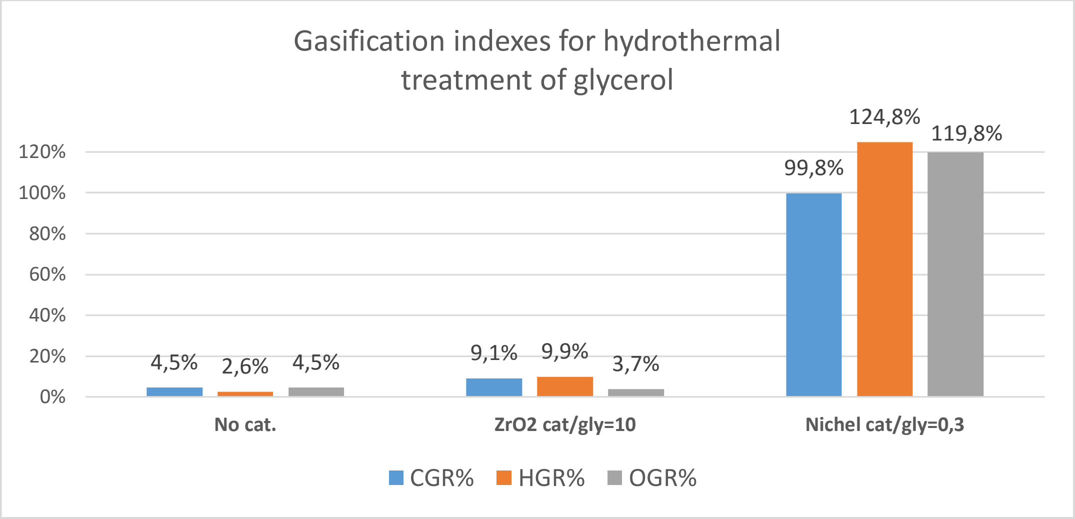


Figure 4.24. Gasification indexes (CGR%, HGR%, OGR%) for hydrothermal treatment of glycerol (gly/water 2,5% w/w) at 375 °C, reaction time 1 hour with different catalyst.

In the absence of the catalyst and with ZrO_2 the amount of gaseous products was very low, in experiments at 375 °C and one hour of treatment time (Figure 4.24). In the presence of nickel, differently, the gasification was complete (99.8% of the carbon atoms initially present in the glycerol were found as gaseous products). From the values of HGR% and OGR% (both greater than 100%) it can be deduced that water was involved in the reaction providing hydrogen and oxygen atoms to gaseous products.

High amounts of H_2 can be obtained by the hydrothermal treatment of glycerol, especially in the presence of nickel catalysts (see Figure 4.25). Carbon dioxide is another reaction product present in abundance, while carbon monoxide is in high concentrations only for the experiments without catalyst and with the zirconium oxide. The mixture of gaseous products also contain small amounts of other light hydrocarbons such as ethane, ethene, propane, propene, n-butane and i-butane.

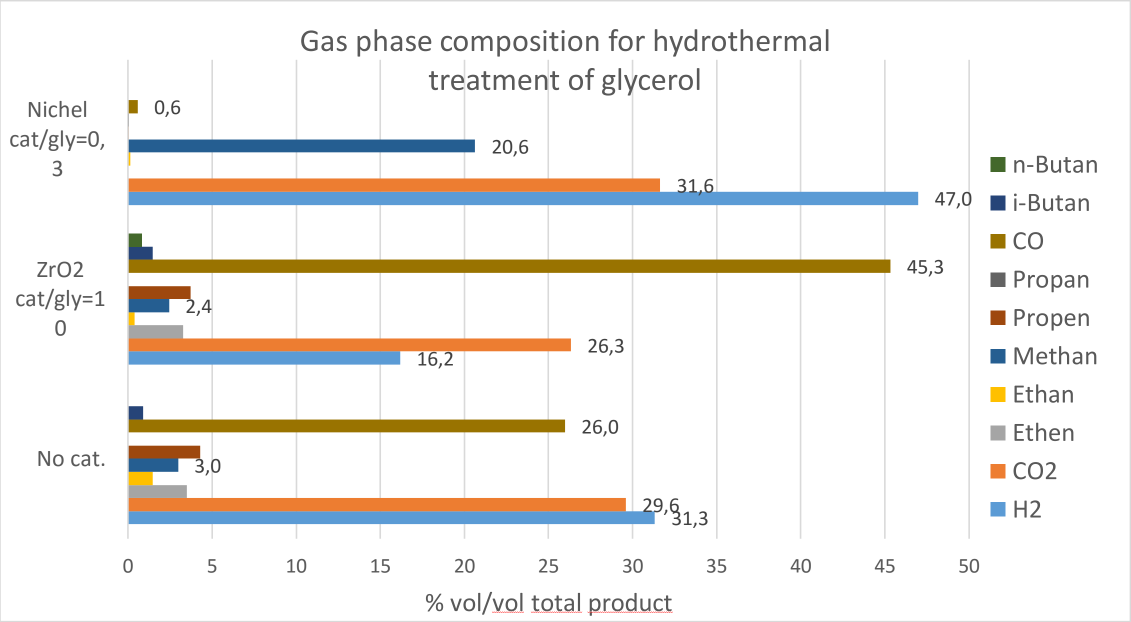


Figure 4.25. Gas phase composition obtained from hydrothermal treatment of glycerol (gly/water 2,5% w/w) in the presence of Raney nickel (mass ratio Raney nickel/gly =0.3 g/g) at 375 °C, reaction time 1 hour.

4.19.1 Analysis of the liquid phase

The HPLC analysis of the aqueous solution indicated the presence of formic acid, acetic acid, acetaldehyde and ethanol, as well as of the eventually unreacted glycerol. In Figure 4.26 the ratio of the mass of each component divided by the initial mass of glycerol are reported. For catalyst free and ZrO_2 catalysed experiments 60% and 68% of the initial glycerol mass respectively remained unreacted. The mass fraction of acetaldehyde reached about 7% for the not catalysed experiment, using ZrO_2 one can get 12% of ethanol, while the other products are all in very small quantities.

By using the Raney nickel small traces of product in aqueous solution were detected (about 2% of the total), confirming in the results of the analysis of the gas phase, i.e. that the gasification was almost complete.

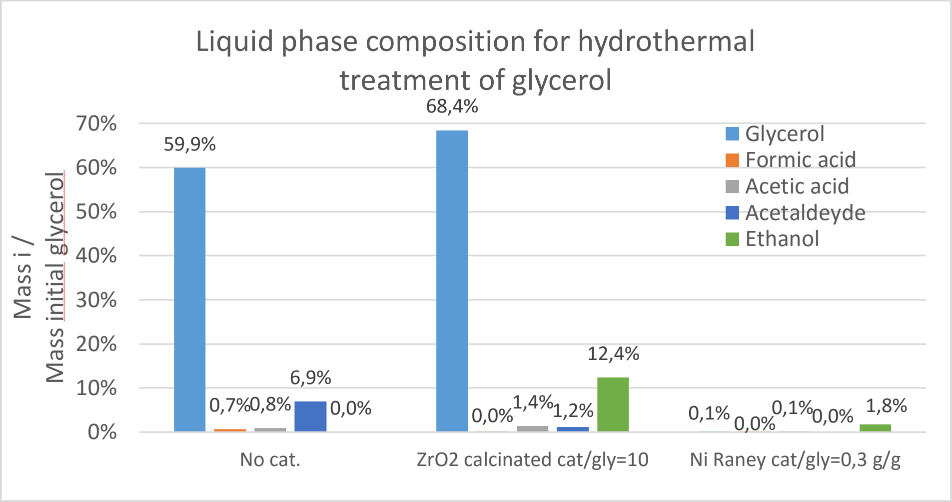
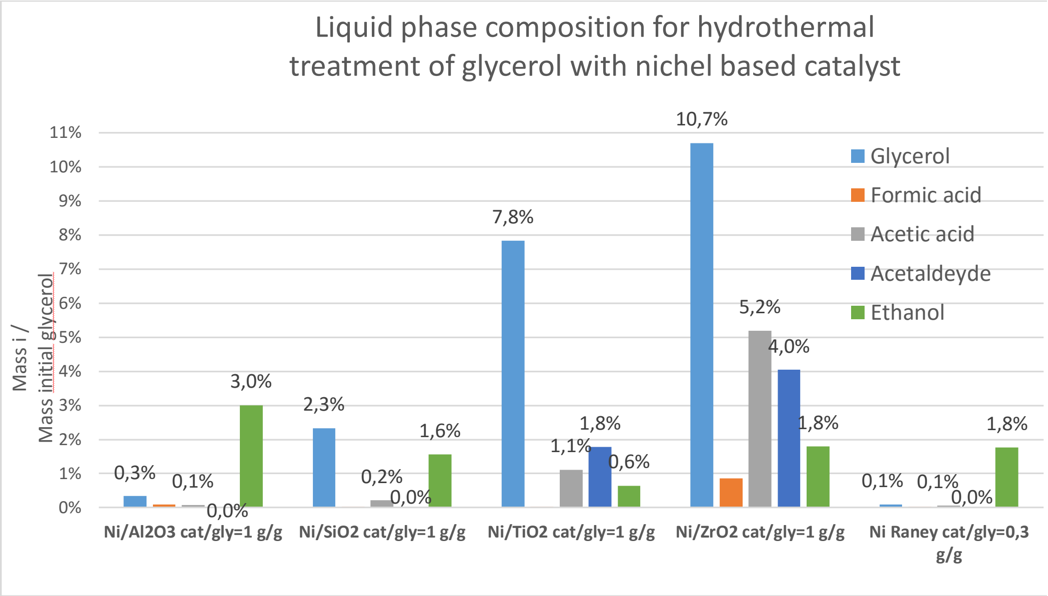


Figure 4.26. Liquid phase composition obtained from hydrothermal treatment of glycerol (gly/water 2,5% w/w) in the presence of different catalyst at 375 °C, reaction time 1 hour.

Other nickel based catalysts supported on Al_2O_3, SiO_2, TiO_2, and ZrO_2 were tested for the hydrothermal gasification of glycerol. The composition of the liquid phase is shown in Figure 4.27: the high loading of nickel in the Ni/Al_2O_3 and Ni/SiO_2 catalysts allowed to convert almost completely the glycerol present in the reactor.



Catalyst	**Nickel Loading (wt%)**
Ni Raney	>90,0%
Ni/ZrO2	5,8 %
Ni/Al2O3	20,0 %
Ni/SiO2	22,0%
Ni/TiO2	5,8 %

Figure 4.27. Liquid phase composition obtained from hydrothermal treatment of glycerol (gly/water 2,5% w/w) in the presence of different catalyst at 375 °C, reaction time 1 hour.

The Ni/TiO_2 and Ni/ZrO_2 catalysts, having a lower loading, left higher residual amount of the substrate in the liquid phase. Higher amount of water soluble compounds were found with these catalysts acetic acid and acetaldehyde, while ethanol was present in the same amount. In general, the relative amounts of each component are difficult to discuss critically, but it can be assumed that the support has a discrete influence on the distribution of the products in the liquid phase.

4.19.2 Effect of treatment time on the gas composition

To search operating conditions that maximizes the hydrogen yield short-term tests were performed. For 15 minutes and 30 minutes of treatment time the composition of the gas is very similar: the highest volume fraction was that of H_2 (about 55%), followed by carbon dioxide (27.5%) and methane (17%) (Figure 4.28). For experiments conducted at 45 and 60 minutes, however, the volumetric fraction in hydrogen decreased, while that of carbon dioxide and methane increased. The increase of the CO_2 concentration can be explained assuming that the gasification increases for long times, while the decrease of H_2 and CH_4 increase is attributable to the methanation reactions. Also in these experiments, light hydrocarbons and carbon monoxide are present in trace amounts.

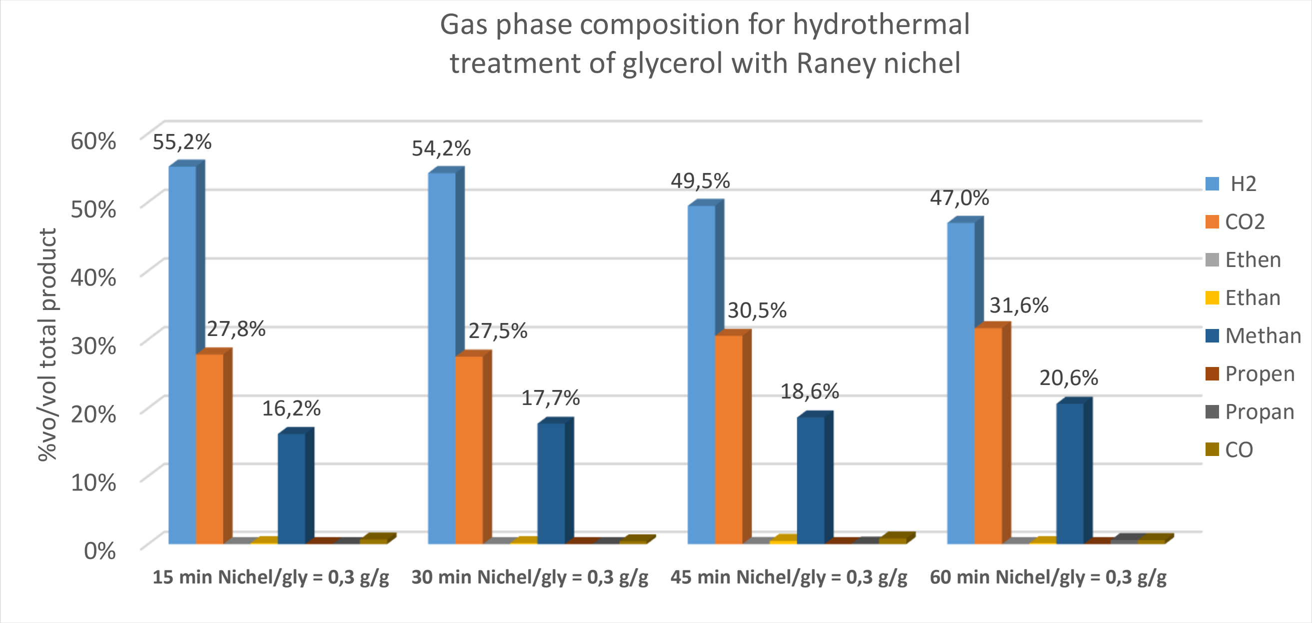


Figure 4.28. Gas phase composition obtained from hydrothermal treatment of glycerol (gly/water 2,5% w/w)in the presence of Raney nickel (mass ratio Raney nickel/gly =0.3 g/g) at 375°C and different reaction time.

4.19.3 Atomic carbon balance

For some tests the carbon atoms in the liquid phase and the gas phase were calculated. The overall balance was obtained from the sum of the number of carbons obtained in the liquid phase and in gas phase, given that apparently no solid phase was found for most samples.

The results in Figure 4.29 show that the sum of the percentage of carbon atoms in the liquid and in gas phase for some tests is close to 100%, while for some testing it reaches only 77%. This result is satisfactory, as regards the analysis of the gas and liquid phases. For tests conducted in the absence of catalyst solid matter on the bottom of the tube was found with eyes. Plausible to think that the balance of carbon atoms does not reach 100% because part of the carbon atoms produces solid products. The solids produced can be estimated as the amount missing to reach 100%; for the tests reported in Figure 4.29 the percentage of solids was 23%.

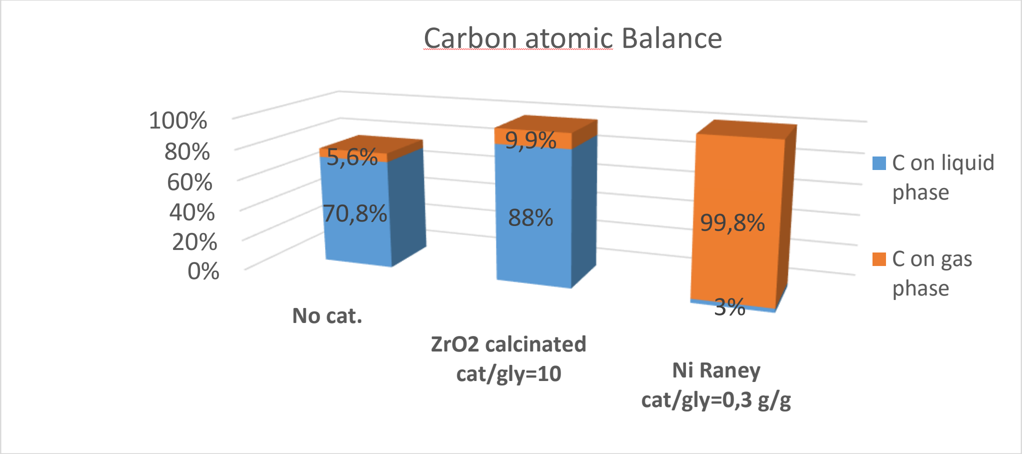


Figure 4.29. Carbon atomic balance obtained for some tests hydrothermal treatment of glycerol (gly/water 2,5% w/w) at different operating conditions.

4.20 Conclusions

The deoxygenation of stearic acid was studied in the presence of water as a reaction medium and with nickel based catalysts. The Raney nickel catalyst, in particular, shows a discrete catalytic activity for the reaction of deoxygenation of stearic acid, because interesting yields of paraffin has been found. In general, the selectivity in heptadecane is not high, especially for total conversions and a significant proportion of reagent is gasifier.

Several operating conditions were studied and 350-375 °C may be indicated as the temperature range which maximizes the yield of alkanes, for the operating conditions adopted. The best results are achieved by treatment times between 30 and 45 minutes. High process severity (i.e. higher treatment times and temperatures) promote the gasification reactions. Also high amount of Raney nickel catalyst lead to gasification of the feed. Only a few tests were carried out varying the catalyst concentration with results suggesting that the amount generally used for this work may be too high. Testing conducted with a catalyst / stearic acid ratio around at 0.05 for example, could improve appreciably the yields of alkanes. Alternatively, it could be interesting to carry out the tests in a continuous process, in order to avoid fragmentation of hydrocarbon products.

Other parameters such as the ratio of stearic acid / water, or the mixing effect can influence the process and should therefore be studied to better identify the best operating conditions.

Nickel was also found an excellent catalyst for the gasification of glycerol in water at sub-critical and supercritical conditions. By treatment of the glycerol, it was possible to obtain a high amount of hydrogen especially for short-time experiments. Increasing the test time (around 45 minutes) complete conversion was reached but the mole fraction of hydrogen decreased since the methanation reactions consumed it. In order to achieve high hydrogen production a continuous process can be considered.

REFERENCES

[1] U. Schuchardt, R. Sercheli, R.M.Vargas. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc., 1998, 9(1), 199-210.

[2] Ma F., Hanna M. A., Biodiesel production: a review, Bioresour. Technol., 1999, 70, 1–15.

[3] Fu J., Lu X., Savage P.E. Catalytic hydrothermal deoxygenation of palmitic acid. Energy Environ. Sci., 2010, 3, 311–317.

[4] A. Corma, G. W. Huber, L. Sauvanaud, P. O'Connor. Processing of biomass-derived oxygenates in the oil refinery: catalytic cracking (FCC) pathways and role of catalysts, J. Catal., 247, 2007, 307.

[5] F. A. Twaiq, N. A. M. Zabidi, A. R. Mohamed, S. Bhatia. Catalytic conversion of palm oil over mesoporous aluminosilicate MCM-41 for the production of liquid hydrocarbon fuels, Fuel Process.Technol. 84, 2003, 105.

[6] A.W. Schwab, G.J. Dystra, E. Selke, S.C. Sorenson, E.H. Pryde. Diesel Fuel from Thermal Decomposition of Soybean Oil. J. Am. Oil Chem. Soc., 65, (1988), 1781.

[7] B. Peng. Transformation of triglycerides and fatty acids into biofuels with sulfur-free catalysts, München, Techn. Univ., Diss., PhD Thesis 2012.

[8] Minami E., Saka S. Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process. Fuel, 2006, 85, 2479–2483.

[9] Mata T. M., Martinsa A. A., Caetano N. S. Microalgae for biodiesel production and other applications: A review. Renewable and Sustainable Energy Reviews, 2010,14, 217–232.

[10] Heilmann S. M., Jader L. R., Harned L. A., Sadowsky M. J., Schendel F. J., Lefebvre P. A., von Keitz M. G., Valentas K. J. Hydrothermal carbonization of microalgae II. Fatty acid, char, and algal nutrient products. Applied Energy, 201, 88, 3286–3290

[11] Miao C., Flores O. M., Davidson S.D., Li T., Dong T., Gao D., Wang Y., Pérez M. G., Chen S. Hydrothermal catalytic deoxygenation of palmitic acid over nickel catalyst. Fuel, 2016, 166, 302–308.

[12] Snåre M., Kubicˇkova´ I., Maki-Arvela P., Eranen K., Murzin D. Y. Heterogeneous Catalytic Deoxygenation of Stearic Acid for Production of Biodiesel. Ind. Eng. Chem. Res. 2006, 45, 5708-5715.

[13] Holliday, R. L., King, W. J., List, G. R. 1997. Hydrolysis of vegetable oils in sub- and supercritical water. Ind. Eng. Chem. Res., 1997, 36 (3), 932–935

[14] Watanabe M., Iida T., Inomata H., Decomposition of a long chain saturated fatty acid with some additives in hot compressed water, Energy Conversion and Management 47, 2006, 3344–3350.

[15] Hollak, S. A. W., Arins M. A., de Jong K. P., van Es D. S. Hydrothermal deoxygenation of triglycerides over Pd/C aided by in situ hydrogen production from glycerol reforming. Chem. Sus. Chem. 2014, 7, 1057 – 1060.

[16] S.E. Hunter, P.E. Savage, Recent advances in acid- and base-catalyzed organic synthesis in high-temperature liquid water, Chemical Engineering Science 59(2004) 4903–4909.

[17] H. Weingartner, E.U. Franck, Supercritical water as a solvent, Angewandte Chemie (International Ed. In English) 44 (2005) 2672–2692.

[18] N. Matubayasi, C. Wakai, M. Nakahara, Structural study of supercritical water. II. Computer simulations, The Journal of Chemical Physics 110 (1999)8000–8011.

[19] E.U. Franck, S. Rosenzweig, M. Christoforakos, Calculation of the dielectric constant of water to 1000-degrees-C and very high-pressures, Berichteder Bunsen-Gesellschaft-Physical Chemistry Chemical Physics 94 (1990)199–203.

[20] K. Heger, M. Uematsu, E.U. Franck, The static dielectric constant of water at high pressures and temperatures to 500 MPa and 550 deg C, Berichte der Bunsengesellschaft für Physikalische Chemie 84 (1980) 758–762.

[21] K. Sue, K. Arai, Specific behavior of acid-base and neutralization reactions in supercritical water, The Journal of Supercritical Fluids 28 (2004) 57–68.

[22] A.V. Bandura, S.N. Lvov, The ionization constant of water over wide ranges of temperature and density, Journal of Physical and Chemical Reference Data 35(2006) 15–30.

[23] M. Boero, T. Ikeshhoji, C.C. Liew, K. Terakura, M. Parrinello, Hydrogen bond driven chemical reactions: beckmann rearrangement of cyclohexanoneoxime into caprolactam in supercritical water, Journal of the American Chemical Society 126 (2004), 6280–6286.

[24] S.J. Halstead, A.J. Masters, A classical molecular dynamics study of the anomalous ionic product in near-critical and supercritical water, Molecular Physics 108 (2010) 193–203.

[25] A. Kruse, N. Dahmen. Water – A magic solvent for biomass conversion, J. of Supercritical Fluids 96 (2015) 36–45.

[26] G.L. Huppert, B.C. Wu, S.H. Townsend, M.T. Klein, S.C. Paspek, Hydrolysisin supercritical water: identification and implications of a polar transition state, Industrial and Engineering Chemistry Research 28 (1989)161–165.

[27] A. Kruse, Supercritical water gasification, Biofuels, Bioproducts and Biorefining 2 (2008) 415–437.

[28] M. Dreher, B. Johnson, A.A. Peterson, M. Nachtegaal, J. Wambach, F. Vogel, Catalysis in supercritical water: pathway of the methanation reaction and sulfur poisoning over a Ru/C catalyst during the reforming of biomolecules, Journal of Catalysis 301 (2013), 38–45.

[29] D.C. Elliott, Catalytic hydrothermal gasification of biomass, Biofuels, Bioproducts and Biorefining 2 (2008) 254–265.

[30] Y. Lu, L. Guo, X. Zhang, C. Ji, Hydrogen production by supercritical water gasification of biomass: explore the way to maximum hydrogen yield and high carbon gasification efficiency, International Journal of Hydrogen Energy 37(2012) 3177–3185.

[31] L. Guo, C. Cao and Y. Lu, Supercritical Water Gasification of Biomass and Organic Wastes, Biomass, Book edited by: Maggie Momba and Faizal Bux, 2010, 202.

[32] Galadima A., Muraza O. Catalytic upgrading of vegetable oils into jet fuels range hydrocarbons using heterogeneous catalysts: A review. Journal of Industrial and Engineering Chemistry, 2015, 29, 12–23.

[33] Shi N., Liu Q., Jiang T., Wang T., Ma L., Zhang Q., Zhang X. Hydrodeoxygenation of vegetable oils to liquid alkane fuels over Ni/HZSM-5 catalysts: Methyl hexadecanoate as the model compound. Catalysis Communication, 2012, 20, 80 - 84.

[34] Wildschut, J., Mahfud, F.H., Venderbosch, R.H., Heeres, H.J. Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. Ind. Eng. Chem. Res., 2009, 48, 10324.

[35] Madsen A.T., Ahmed E.H., Christensen C.H., Fehrmann R., Riisager A. Hydrodeoxygenation of waste fat for diesel production: Study on model feed with Pt/alumina catalyst. Fuel, 2011, 90, 3433.

[36] Murata K., Liu Y., Inaba M., Takahara I. Production of synthetic diesel by hydrotreatment of jatropha oils using Pt-Re/H-ZSM-5 catalyst. Energ. Fuel., 2010, 24, 2404.

[37] Veriansyah B., Han J.Y., Kim S.K., Hong S.-A., Kim Y.J., Lim J.S., Shu Y.-W., Oh S.G., Kim J. Production of renewable diesel by hydroprocessing of soybean oil: Effect of catalysts. Fuel, 2012, 94, 578.

[38] M. Mohammad, T. Kandaramath Hari, Z. Yaakob, Y. Chandra Sharma, K. Sopian. Overview on the production of paraffin based-biofuels via catalytic hydrodeoxygenation. Renew. Sust. Energ. Rev., 2013, 22, 121.

[39] Lestari S., Mäki-Arvela P., Eränen K., Beltramini J., Max Lu G.Q., Murzin D.Y. Diesel-like hydrocarbons from catalytic deoxygenation of stearic acid over supported Pd nanoparticles on SBA-15 catalysts. Catal. Lett., 2010, 134, 250.

[40] Y. Yoshimura, M. Toba, T. Matsui, M. Harada, Y. Ichihashi, K.K. Bando, et al. Active phases and sulfur tolerance of bimetallic Pd-Pt catalysts used for hydrotreatment. Appl. Catal. A, 2007, 322, 152.

[41] S. Harnos, G. Onyestyák, D. Kalló. Hydrocarbons from sunflower oil over partly reduced catalysts. Reac. Kinet. Mech. Cat., 2012, 106, 99.

[42] R. Prins, V. De Beer, G. Somorjai. Structure and Function of The Catalyst and The Promoter In Co—Mo Hydrodesuifurization Catalysts. Catal. Rev. Sci. Eng., 1989, 31, 1.

[43] X. Ma, K. Sakanishi, I. Mochida. Hydrodesulfurization reactivities of various sulfur compounds in diesel fuel. Ind. Eng. Chem. Res., 33, 1994, 218.

[44] C.H. Zandonai, P.H. Yassue-Cordeiro, S.B. Castellã-Pergher, M.H.N.O. Scaliante, N.R.C. Fernandes-Machado. Production of petroleum-like synthetic fuel by hydrocracking of crude soybean oil over ZSM5 zeolite – Improvement of catalyst lifetime by ion exchange. Fuel, 2016, 172, 228–237.

[45] T. Blasco, A. Chica, A. Corma, W.J. Murphy, J. Agúndez-Rodríguez, J. Pérez-Pariente. Changing the Si distribution in SAPO-11 by synthesis with surfactants improves the hydroisomerization/dewaxing properties. J. Catal., 2006, 242, 153.

[46] Pacchioni G., Ketonization of Carboxylic Acids in Biomass Conversion over TiO2 and ZrO2 Surfaces: A DFT Perspective. ACS Catal., 2014, 4, 2874−2888.

[47] Barteau, M. A., Organic Reactions at Well-Defined Oxide Surfaces M. A. Chem. Rev. 1996, 96, 1413−1430.

[48] A. Corma, G.W. Huber, L. Sauvanaud, P. O'Connor. Processing biomass-derived oxygenates in the oil refinery: Catalytic cracking (FCC) reaction pathways and role of catalyst. J. Catal., 247, 2007, 307.

[49] D. Kubička, L. Kaluža. Deoxygenation of vegetable oils over sulfided Ni, Mo and NiMo catalysts. Appl. Catal. A, 372, 2010, 199.

[50] L. Kaluža, D. Gulková, Z. Vít, M. Zdražil. Effect of support type on the magnitude of synergism and promotion in CoMo sulphide hydrodesulphurisation catalyst. Appl. Catal. A, 324, 2007, 30.

[51] J. Horáček, Z. Tišler, V. Rubáš, D. Kubička. HDO catalysts for triglycerides conversion into pyrolysis and isomerization feedstock. Fuel, 121, 2014, 57.

[52] Santillan-Jimenez, E., Morgan, T., Lacny, J., Mohapatra, S., Crocker, M. Catalytic deoxygenation of triglycerides and fatty acids to hydrocarbons over carbon-supported nickel. Fuel, 103, 2013, 1010–1017.

[53] Vardon, D.R., Sharma, B.K., Jaramillo, H., Kim, D., Choe, J.K., Ciesielski, P.N., Strathmann, T.J. Hydrothermal catalytic processing of saturated and unsaturated fatty acids to hydrocarbons with glycerol for in situ hydrogen production. Green Chem., 16 (3), 2014, 1507–1520.

[54] Manfro, R.L., Da Costa, A.F., Ribeiro, N.F.P., Souza, M.M.V.M. Hydrogen production by aqueous-phase reforming of glycerol over nickel catalysts supported on CeO2. Fuel Process Technol, 92 (3), 2011, 330–335.

[55] Iriondo A., Barrio V. L., Cambra J. F., Arias P. L., Guemez M. B., Navarro R. M., Sànchez-Sànchez M. C., Fierro J. L. G. Hydrogen Production from Glycerol Over Nickel Catalysts Supported on Al2O3 Modified by Mg, Zr, Ce or La. Top Catal. (2008) 49:46–58.

[56] Trimm D.L. Coke formation and minimisation during steam reforming reactions. Catal. Today, 1997, 37:233.

[57] Davda R.R., Shabaker J.W., Huber G.W., Cortright R.D., Dumesic J.A. Aqueous-phase reforming of ethylene glycol on silica-supported metal catalysts. Appl. Catal. B. Environm., 2003, 43:13.

[58] Shabaker J.W., Davda R.R., Huber G.W., Cortright R.D., Dumesic J.A. Aqueous-phase reforming of methanol and ethylene glycol over alumina-supported platinum catalysts. J. Catal., 2003, 215:344.

[59] Parmaliana, A., Arena, F., Frusteri, F., Coluccia, S., Marchese, L., Martra, G., Chuvilin, A. Magnesia-Supported Nickel Catalysts: II. Surface Properties and Reactivity in Methane Steam Reforming. J. Catal., 1993, 141:34.

[60] Souza MMV, Schmal M. Production of synthesis gas from natural gas using ZrO2-supported platinum. Stud. Surf. Sci. Catal., 2004, 147:133.

Chapter 5

DEVELOPMENT OF CONTINUOUS REACTION SYSTEM FOR HYDROTHERMAL GASIFICATION OF BIOMASS AND MODEL COMPOUND

5.1 Introduction

As described in Chapter 4, hydrothermal processes constitute an interesting possibility for the conversion of renewable biomass with high water content for the formation of chemical energy carriers (fuels) or chemicals. Water has a key role in such processes and can play the role as reaction medium, reagents, catalyst precursor or catalyst. The most important advantage of the hydrothermal treatment is that wet biomass can be converted directly so avoid the drying step that requires high-energy cost [1, 2].

The hydrothermal gasification process (HTG) consists in the treatment of organic compounds in the presence of water at a temperature above 400 ° C and without introduction of oxygen or air in the reaction medium. The reaction generally produces valuable gaseous products, such as hydrogen and methane, but can also produce bio-oils and solid compounds.

Just because in HTG, water is used in above its critical point (374 °C, 22.1 MPa), the technology is more properly called "supercritical water gasification" (SCWG).

The high reactivity of the polar components of biomass in hot compressed water and the properties change with temperature of this solvent are the key factors that indicate water as an attractive material for various applications.

In this chapter a brief bibliographic collection on SCWG technology is provided. The catalysts and the most suitable operating conditions for this technology are still the subject of study.

The activity of this work has focused on the realization of a continuous system in order to study some aspects that in the batch configuration can not be addressed. A continuous configuration, in fact, allows to conduct the reaction in a short time and to realize of very different fluid dynamic conditions compared to the discontinuous configuration.

Some experiments on model compounds of triglycerides have also been conducted and presented.

5.2 Feedstock

The type of raw material fed to the process generally affects the performance of SCWG. Two different types of raw materials are typically used in R&D laboratories to evaluate the effectiveness of the SCWG process: model compounds and real biomass.

The gasification of model compounds can be studied both as a single component or mixtures of different molecules, to determine the possible interactions between the various reactants during the gasification process. The real biomass is more difficult to study because it has a more complex structure and a more heterogeneous composition.

5.3 The role of catalysts in SCWG

The gasification of organic substances in SCW without catalyst has been widely studied and reported in the literature. SCWG without catalyst usually produces a greater amount of CO due to the low rate of water shift reaction. Not catalysed SCWG processes requires a very high temperature to achieve acceptable conversions (e.g. > 600°C) [3].

At temperatures of about 700 °C, the reactions are fast and a complete gasification is obtainable in the absence of catalysts or by adding only carbon or alkali salts to inhibit tar formation [4].

For supercritical water at a moderate temperature (374-550 °C), transition metal catalysts, such as nickel and ruthenium are generally used to increase the kinetics of the gasification reaction [4].

In subcritical region, only highly active metal catalysts such as Raney nickel and platinum are useful for the gasification of organic oxygenated compounds [5].

The heterogeneous catalysts used for the gasification are classified into three main groups: activated carbon catalysts, metals and oxides. Metal catalysts are further divided into supported and unsupported catalysts [3].

5.4 Current status of the catalytic SCWG

The activated carbon is obtained from natural sources such as wood, coal and shells. They can withstand high temperature in an inert environment, in contact with vapour or reducing gases. It is often used as catalytic support but also as a catalyst itself. The type of preparation of the active carbons can address toward a particular structure, specific chemical-physical characteristics and high surface area [3].

Thanks to these characteristics the activated carbon are also used in hydrogenation reactions or in the production of fine chemicals.

The literature indicates the active carbon as the best known heterogeneous catalyst for very high temperatures (over 600 °C) [6]. The commercial catalysts used for the SCWG process are the same as those used for hydrogenation processes (for example Raney nickel), methane steam reforming process and naphtha production (for example Ni/Al_2O_3). The catalysts based on noble metals such as Ru, Pt are often supported on Al_2O_3 or and C, which are widely used for the high catalytic activity and ease of use [3].

In commercial catalysts noble metals are sometimes dispersed on the support with high loadings (30 - 50%), providing a greater number of catalytic sites to the mass of active metal.

Some catalytic systems designed to improve the resistance of the catalyst or to increase the selectivity. Some studies show that the addition of Sn on the surface of Raney nickel improves the selectivity of the process [7].

Only few studies are dedicated to the production of catalytic systems suitable for the SCWG technology. The commercial catalysts still manage to be sufficiently active for the process and provide useful information for the study of the catalytic process.

5.5 Transition metals

In SCWG process, metal catalysts have been employed both as supported and not supported. In the context of catalytic SCWG, supported metal catalysts can be in form of powders and wires with low specific surface area and skeletal structures (i.e. Raney catalysts, see also below). These metals and metal oxides in powder or wire form have been used only in order to demonstrate the catalytic activity of the catalysts. Because of the low surface areas of these catalysts they cannot be applied on an industrial scale.

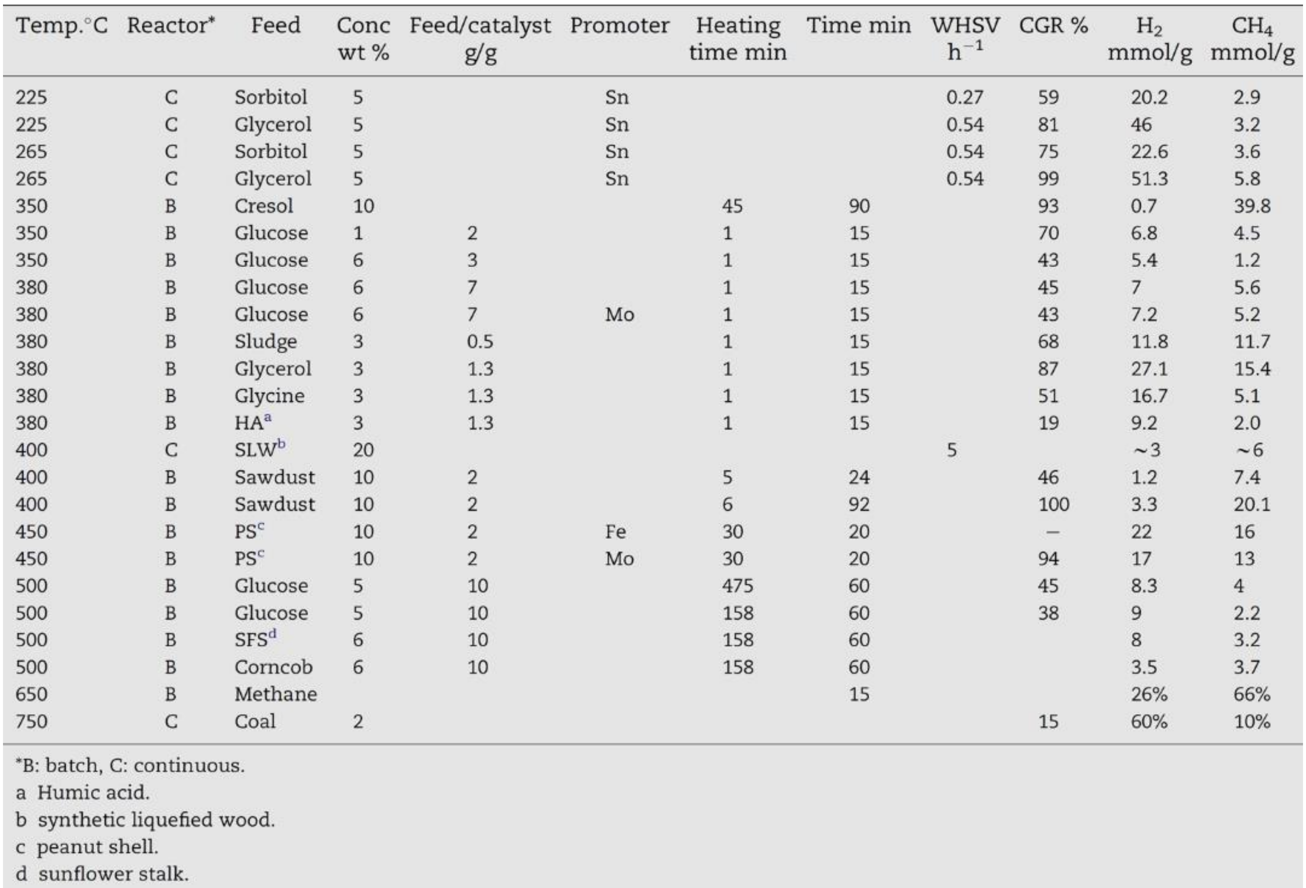
Nickel [8], nickel oxide [9], ruthenium [10], ruthenium oxide [9], and platinum [11] have been tested to catalyse the gasification of organic substances in supercritical water. Pt-black, which has an appreciable surface area, showed a remarkable turnover frequency (TOF) for gasification of model compounds even at low temperatures [11]. However, the price of noble metals is prohibitive for use in large scale.

Raney nickel catalysts (skeletal) are prepared by leaching aluminium from an aluminium metal alloy, resulting in the formation of the remaining target metal with a spongy structure. The remaining material contains typically few percentages of aluminium [12]. The ratio Ni/Al in the initial alloy plays an important role on the activity of such catalysts. Ni_2-Al_3 (59% Ni) and Ni-Al_3 (42% Ni) are the two most commonly used proportions. The Raney nickel is among the cheapest catalysts [13] in SCWG and the most active [14].

The main problem related to the use of Raney nickel is that it oxidizes easily when exposed to oxidizing environment or even in contact with supercritical water for a long period. As the nickel oxide does not have catalytic properties for the reactions in SCWG, the oxidation of the catalyst must be avoided [15]. However, once oxidation occurs, it is possible to regenerate the catalyst by treating it in a reducing environment. In figure 5.1, the results of some compounds treated in SCWG catalysed by Raney nickel are reported. Fresh skeletal nickel catalyst has a remarkable ability to cleave the C-O bonds, but also catalyses the methanation reactions (see chapter 4) so that large amounts of hydrogen can be consumed.

The methanation reactions are favoured at low temperature and high concentrations. To increase the selectivity into hydrogen is necessary to adopt low residence times inside the reactor, very low concentrations of reagent and high temperature. It has been shown that the addition of promoters in small amounts, such as Sn, Mo and Fe on the surface of Raney nickel catalyst may improve the selectivity to hydrogen [7]. Another strategy suggested to the selectivity to hydrogen, it is to use a specific catalytic support; for example, the addition of ceria may improve the selectivity of the catalyst [16].

A wide variety of supported nickel catalysts have been used to catalyse SCWG. The influence of the support material has minimal effect on the reaction with respect to that of the supported metals. In fact, no support or promoter has been found so far to be able to significantly improve the selectivity for hydrogen supported nickel catalysts [3].

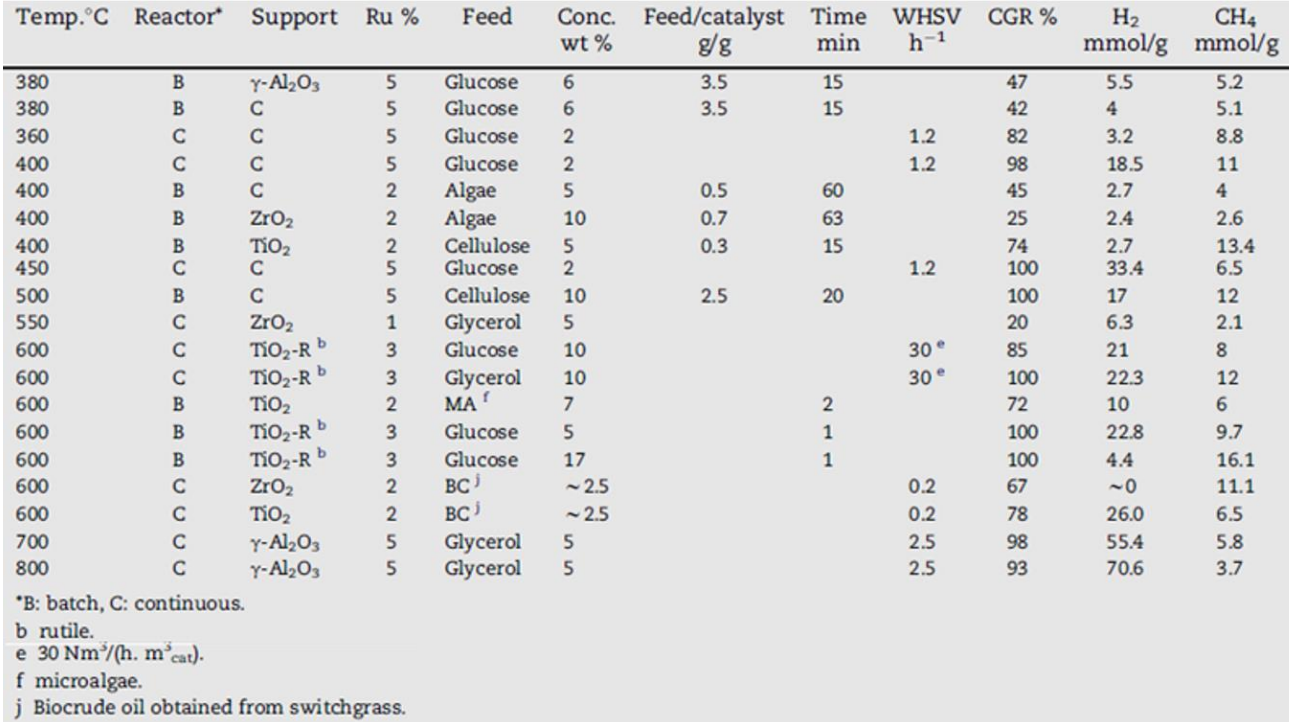


Temp.°C	Reactor*	Feed	Conc wt %	Feed/catalyst g/g	Promoter	Heating time min	Time min	WHSV h^{-1}	CGR %	H_2 mmol/g	CH_4 mmol/g
225	C	Sorbitol	5		Sn			0.27	59	20.2	2.9
225	C	Glycerol	5		Sn			0.54	81	46	3.2
265	C	Sorbitol	5		Sn			0.54	75	22.6	3.6
265	C	Glycerol	5		Sn			0.54	99	51.3	5.8
350	B	Cresol	10			45	90		93	0.7	39.8
350	B	Glucose	1	2		1	15		70	6.8	4.5
350	B	Glucose	6	3		1	15		43	5.4	1.2
380	B	Glucose	6	7		1	15		45	7	5.6
380	B	Glucose	6	7	Mo	1	15		43	7.2	5.2
380	B	Sludge	3	0.5		1	15		68	11.8	11.7
380	B	Glycerol	3	1.3		1	15		87	27.1	15.4
380	B	Glycine	3	1.3		1	15		51	16.7	5.1
380	B	HA[a]	3	1.3		1	15		19	9.2	2.0
400	C	SLW[b]	20					5		~3	~6
400	B	Sawdust	10	2		5	24		46	1.2	7.4
400	B	Sawdust	10	2		6	92		100	3.3	20.1
450	B	PS[c]	10	2	Fe	30	20		—	22	16
450	B	PS[c]	10	2	Mo	30	20		94	17	13
500	B	Glucose	5	10		475	60		45	8.3	4
500	B	Glucose	5	10		158	60		38	9	2.2
500	B	SFS[d]	6	10		158	60			8	3.2
500	B	Corncob	6	10		158	60			3.5	3.7
650	B	Methane					15			26%	66%
750	C	Coal	2						15	60%	10%

*B: batch, C: continuous.
a Humic acid.
b synthetic liquefied wood.
c peanut shell.
d sunflower stalk.

Figure 5.1. Result of catalytic SCWG using Raney nickel catalyst no support [3].

In addition, catalysts based on ruthenium are referred to as good catalysts for SCWG. Similarly to other noble metals, ruthenium is resistant to high temperatures, sintering and oxidation. In figure 5.2 some results of SCWG catalysed by ruthenium are shown. Often the catalyst is supported on carbon, titanium oxide or alumina. In particular, ruthenium-based catalysts supported on titanium rutile [8] or carbon [17] seem to have a good long-term stability.



Temp.°C	Reactor*	Support	Ru %	Feed	Conc. wt %	Feed/catalyst g/g	Time min	WHSV h^{-1}	CGR %	H_2 mmol/g	CH_4 mmol/g
380	B	γ-Al_2O_3	5	Glucose	6	3.5	15		47	5.5	5.2
380	B	C	5	Glucose	6	3.5	15		42	4	5.1
360	C	C	5	Glucose	2			1.2	82	3.2	8.8
400	C	C	5	Glucose	2			1.2	98	18.5	11
400	B	C	2	Algae	5	0.5	60		45	2.7	4
400	B	ZrO_2	2	Algae	10	0.7	63		25	2.4	2.6
400	B	TiO_2	2	Cellulose	5	0.3	15		74	2.7	13.4
450	C	C	5	Glucose	2			1.2	100	33.4	6.5
500	B	C	5	Cellulose	10	2.5	20		100	17	12
550	C	ZrO_2	1	Glycerol	5				20	6.3	2.1
600	C	TiO_2-R [b]	3	Glucose	10			30 [e]	85	21	8
600	C	TiO_2-R [b]	3	Glycerol	10			30 [e]	100	22.3	12
600	B	TiO_2	2	MA [f]	7		2		72	10	6
600	B	TiO_2-R [b]	3	Glucose	5		1		100	22.8	9.7
600	B	TiO_2-R [b]	3	Glucose	17		1		100	4.4	16.1
600	C	ZrO_2	2	BC [j]	~2.5			0.2	67	~0	11.1
600	C	TiO_2	2	BC [j]	~2.5			0.2	78	26.0	6.5
700	C	γ-Al_2O_3	5	Glycerol	5			2.5	98	55.4	5.8
800	C	γ-Al_2O_3	5	Glycerol	5			2.5	93	70.6	3.7

*B: batch, C: continuous.

b rutile.

e 30 $Nm^3/(h. m^3_{cat})$.

f microalgae.

j Biocrude oil obtained from switchgrass.

Figure 5.2. Result of catalytic SCWG using supported nickel catalyst [3].

Unfortunately, ruthenium-based catalyst are very sensitive to poisoning by sulfuric compounds, even when these last are present in low concentrations [17]. Other precious metals such as platinum [11] and palladium [18] were also found to be active in catalysing the decomposition reactions in SCW, or example in the deoxygenation of fatty acids to produce hydrocarbons (see previous chapter).

5.6 Oxides

Some metal oxides, such as CaO [19], ZrO_2 [20], and CeO_2 [21] and Fe_2O_3, were tested as SCWG catalysts. CaO seems to have no very catalytic activity for the reaction, but it manages to capture the carbon dioxide produced causing an increase in the concentration of hydrogen in the gas phase [19]. Instead, ZrO_2 was found to be a discrete catalyst for the gasification of glucose with H_2 yield twice as much as that without catalyst at 440°C and 10 minute [20].

CeO_2 did not show interesting catalytic properties [17], while Fe_2O_3 mixed with other oxides (such as CaO and Na_2O) can probably accelerate the water gas shift reaction [22].

5.7 Types of reactors

Several reactor systems have been used to study the catalytic gasification in supercritical water, including fixed bed, CSTR, quartz capillaries and tubular reactors. In addition, some studies have reported application of fluidized beds [23]. It was shown that tar and char formation is accelerated when the heating of the biomass is maintained at a moderate temperature for a prolonged time. Therefore, in order to avoid the formation of tar and char or minimize this effect, the heating rate should be as high as possible.

Some researchers have used capillary quartz tube because their resistance to high temperatures and pressures allows quick heating [24]. On the other hand, however, these systems do not allow the adoption of fixed catalyst bed because of very small diameter; for this reason, they have been mainly used for non-catalysed tests [3].

The continuous-flow reactors used in SCW experiments allow studying additional aspects of biomass gasification, e.g. the effect of Reynolds number, high heating rate, short residence time, and constitute a more realistic approach for huge production of commodities, such as biofuels. However, there are several practical difficulties to be faced, including the pumping of slurry in precise quantities at high pressure, problems of fouling and clogging of pipes caused by the heavy products and the presence of salts, and the rapid heating of the feed entering into the reactor.

5.8 Experimental section

The laboratory-scale continuous plant developed for the biomass conversion in supercritical water is shown in Figure 5.3. The main parts of the system are the feedstock suspension/slurry and water supply section, the water preheating and the reaction section, the cooling section and the expansion of the product stream outcoming from the reactor and the separation system.

The liquids are moved by metering piston pumps, which have a maximum flow rate of 10 ml/min and the ability to control the flow with accuracy 0.01 ml/min at pressures up to 400 bar. For the experiments in which model compounds have been used (for example, glycerol, glucose, etc.), as they are water soluble, it is possible to feed the water solution directly in the system by using the metering pump, thus bypassing the piston. For the preheater of the process water a 1/8 " outside diameter (OD), 0.040” inside diameter (ID) tube was used with a length of 12 meters, while the reactor was constituted by a 9/16" OD, 1/4” ID tube with a length of 30 cm and a total volume of 9.6 cm^3. All these components have mechanical properties adequate to operate in conditions higher than those for which the system has been designed, which are 500 °C and 30 MPa as maximum values.

In between, the water preheater and reactor a "T" connection is situated which has the function of mixing the supercritical water coming from the preheating section with the feedstock solution/slurry, before entering into the reactor.

To reach the high temperature two ceramic radiant heaters have been installed which allows high heat flux. The heaters have been arranged to heat also the mixer in addition to the preheater and the reactor tube.

The reactor outlet stream is rapidly cooled down via heat exchange with tap water. A simple relief valve is used to expand the product stream the operating pressure to atmospheric.

A cylinder was connected to the relief valve outlet to collect and separate the gas phase from the condensed ones. The gaseous products are then filtered to remove water and other liquids possibly dragged out from the separator, and measured by a flow meter. The separator also has the function of separate the aqueous phase from organic liquid (and solids, if present) that may be formed by the reaction, via settling.

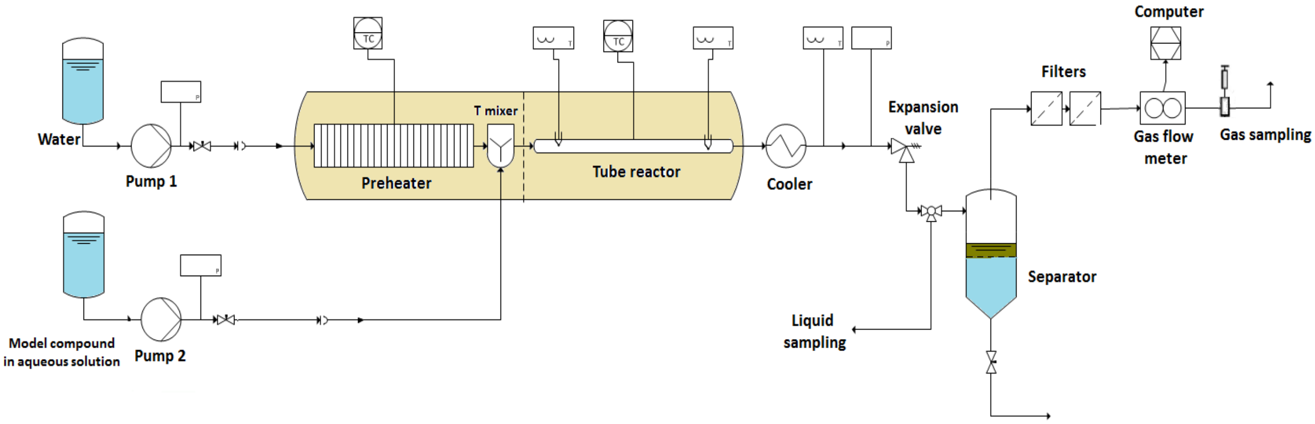


Figure 5.3. Flow sheet of the plant in continuous laboratory scale developed for the treatment of biomass in supercritical water.

5.9 Management and control of the system

The flow sheet in Figure 5.3 the main parts of the acquisition and system control are also shown. The dosing pumps are equipped with a pressure transducer, which indicates the delivery pressure. For increased accuracy and redundancy of the pressure, indication precision pressure gauges were installed in each supply line, which are also provided with non-return valves for safety reasons. The pumps are also equipped with high-pressure block for the protection of all system components. As an example, for experimental tests performed at 26 MPa, the pressure block was set to 27 MPa.

As mentioned, the pressure control has been obtained with the use of a relief valve placed after the cooling section. The desired operative pressure inside the system can be by this adjusted by simply opposing the force generated by the process fluid with the adjustable elastic force of a suitable spring of the device. When the force of the fluid exceeds the spring force of the valve immediately opens and the fluid can pass through it; due to the fluid outcome, the pressure inside the system decreases a few so that the relief closes and the system pressure increases again, due to the continuous feeding. This cyclic behaviour with a small pressure variation and flow stopping, so that the flow regime can be assumed as continuous. The relief valve also functions as the expansion valve because it is able to cause a drop of the fluid pressure from about 26 MPa to atmospheric pressure.

For each of the two ceramic heater of the preheater-mixer-reactor zone (hot zone) a PID controller was used. The controlled variables are the temperature of the preheater pipe wall and the reactor wall respectively. For each PID, control parameters were specifically optimized.

The process temperatures were measured using sensors inserted in the pipe in direct contact with the fluid. Two sensors were installed in the initial and final part of the reactor to get information on the reactor thermal profile and after the cooling section. For all controlled and measured temperatures, K-type thermocouples were used.

The gas flow produced during continuous operation is filtered by two cartridge filters capable to bring down particles with diameter of up to 5 microns and to 0.01 microns, respectively. The particles are generally present in the gas stream as entrained liquid droplets that may damage the operation of the electronic flow meter.

The flow meter used is an electronic mass flow meter capable of estimating with high precision product gas in a flow range of 0.8 - 150 ml/min. The flow value is provided with respect to a reference gas; therefore, it is necessary to know the exact composition of the gas in order to correctly calculate the real flow of the obtained gas phase. The device generates an analogic signal, which is converted to a digital one recordable on a computer, so that it is possible to record the values of the flow rate for the duration of the experimental testing.

5.10 Test procedure and analytical techniques

The procedure of the experimental tests required considerable experimental work, because of the severe operating conditions and the complexity of the experimental apparatus.

Initially the system is fed only with pressurized (26 MPa) water through the preheater at the desired flow rate for the test. An initial temperature set point of 250 °C recommended and it is reached in about 1 h at constant water flow. For higher operative temperatures, the increase must be gradual to avoid excessive thermal gradients and overshooting. Therefore, the set point above 250 °C must be varied in steps of 100 °C; this thermal step is usually achieved in about 20 min at constant feeding flow. For a test at 500 ° C, the thermal start-up time is then about 90 minutes.

The experimental tests have shown that at steady state conditions, the temperature of the outer wall of the tubes should be about 50 °C higher than the temperature of the processed fluid. Therefore, for a test where the desired temperature is 500 °C the furnace must reach 550 °C. In general, this temperature difference (ΔT) depends on the operating conditions (temperature, flow rates) and could therefore adjusted manually.

The adopted flow rates depend on the desired residence time inside the reactor and in general vary from 1.5 to 6 ml/min for the preheated water flow rate and 0.2-1.5 ml/min for the feedstock solution. The residence time was estimated as the ratio between the reactor volume and the volumetric flow rate of the fluid flowing through the reactor:

$$\tau = \frac{V_R}{Q_R} = \frac{V_R * \rho_R}{W} \; ; \qquad\qquad \rho_R = f(T, P)$$

For the calculation of the residence time, the system density at the process conditions must be considered. As an assumption, only the density of the water is considered, thus neglecting the presence of the feedstock.

The diagram of the figure 5.4 shows the variation of the density of water by varying temperature and pressure.

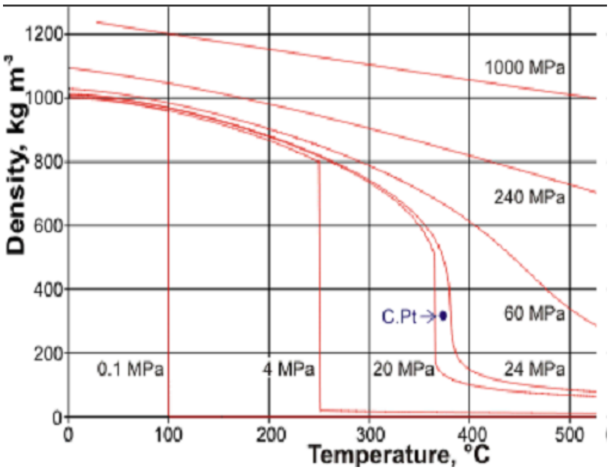


Figure 5.4. Water density with varying temperature and pressure.

The range of residence times applicable with the continuous plant, therefore, varies from 5 to about 30 seconds.

The mass concentration in the reactor was calculated taking into account the concentration of the reagent solution fed and the effect of the diluent water flow through the preheater. The reagent solution has a known concentration obtained from the ratio between the total mass of reagent and the total mass of the solvent (M_i / M_s), and is fed to the plant with mass flow rate w_2; the mass of fed compound in the time unit is then:

$$Mass\ \ flow\, rate\, of\, reactant = \frac{M_i}{M_s} * w_2$$

Indicating with "w_1" the flow of water that passes through the preheater, the concentration of reagent in the inlet of the reactor is calculated with the following formula:

$$Concentration\ in\ the\ reactor = \left(\frac{M_i}{M_s} * w_2\ \right)/(w_1 + w_2)$$

The Reynolds number was calculated using the formula valid for fluid motions in pipes:

$$Reynolds = \frac{\rho_f * v_f * D_r}{\mu_f}$$

Where ρ_f, v_f, μ_f are the density, the velocity and the viscosity of the fluid, respectively, inside the reactor under the operating conditions adopted, while D_r represents the internal diameter of the reactor pipe.

A carbon recovery balance is here considered as the ratio between the sum of carbon masses obtained in the gas phase and the liquid divided by the mass of carbon fed in the time unit:

$$\%\, C = \frac{C_{gas}\ \ + \left(C_{aqueous} + C_{organic}\,\right)}{C_{feed}} * 100$$

This calculation allows to check the reliability of the analysis and of the test procedure, and to give an indication of the amount of the possible solid products that may form during the reaction. The percentage of carbon in solids is then calculated by difference as the aliquot for the completion of the carbon balance:

$$\%C_{solido}\ = 100 - \%C$$

It must be noted that the mass balance for these processes can be done referring to the carbon atoms, but in principle not to the total mass of feedstock or to hydrogen or oxygen atoms. The reason lies in the fact that the water, in addition to the solvent role, is also a reagent and thus hydrogen and oxygen present in the products can also come from the reaction of supercritical water molecules. Nevertheless, a parameter is often used in the literature, which is named gasification efficiency and defined as the ratio between the mass of gaseous obtained products and the mass of fed reactant.

$$\%GE = \frac{Mass\ of\ gas\ product}{Mass\ of\ feed} * 100$$

According to the considerations above, this parameter can in principle assume values even higher than 100%.

As mentioned in the previous chapter, other gasification indices reported in the literature are also present and related to carbon, hydrogen and oxygen, such as the gasification ratios (GRs) below:

$$\%CGR = \frac{Mol\ Carbon\ gas}{Mol\ Carbon\ feed} * 100; \qquad \%HGR = \frac{Mol\ Hydrogen\ gas}{Mol\ Hydrogen\ feed} * 100;$$

$$\%\ OGR = \frac{Mol\ Oxygen\ gas}{Mol\ Oxygen\ feed} * 100$$

Even in this case, hydrogen and oxygen gasification ratios can in principle reach values higher than 100%, while for the CGR the maximum is 100%.

When the system reaches the steady state temperature, the feedstock solution can be fed by operating the second dedicated pump. A suitable ratio between the preheated water and the feedstock solution is used so that the variation between the temperature of the former and that of the mixture entering the reactor is acceptable, this last being the target one desired for the process.

The sampling of the liquid phases can be operated in the separator at the end of the experiment, or by using a three-way ball valve to switch the depressurized product stream toward another collecting reservoir (vial) in a short time interval (e.g. 5 min).

The gas is sampled from the stream entering the flow meter, using a gas tight 250 µl syringe for GC analysis.

To the aqueous solution to a total organic carbon analysis (TOC) it has been arranged to estimate the amount of residual carbon in the liquid. Shimadzu TOC-L Series analyser was used.

For the analysis of the gas phase it was used an apparatus Agilent 7890B Gas Chromatograph (GC) equipped with Supelco matrix 60/80 Carboxen-1000 support, (length 4.6 m, external diameter of 1/8 in. internal diameter of 2.1 mm), using a Thermal Conductivity Detector (TCD) and helium 5.0 as carrier gas. Oven temperature was set at 35 °C for 5 min, and then it was increased with a heating rate of 5 °C/min up to 225 °C and maintained for 10 min.

The quantification of the compounds instead be obtained using Agilent 7890B Gas Chromatograph (GC) equipped with a capillary column Restek Stabilwax, (length 30 m, external diameter of 0.25 mm, internal diameter of 0.25 mm) using a Flame Ionization Detector (FID) and helium 5.0 as carrier gas.

5.11 Results and Discussion

The layout of the continuous system as described in the experimental section is the result of numerous transformations and improvements. Among the most important changes made to the system during the construction phase it should be mentioned the arrangement of the hot zone elements (preheater, static mixer, reactor) inside the electric heaters. Initially, the heaters were shorter and could not irradiate the mixer. The volume between the two heaters remained therefore a large heat dissipation zone and this heavily influenced the thermal profile inside the reactor: the water passing through the preheater reached the desired temperatures, but suffered an excessive cooling in the not irradiated zone, even adopting good insulating materials.

Some tests were performed feeding only water, to study the thermal behaviour of the system and optimize the temperature control. With the original layout, a minimum difference of 10-20 °C between the inlet and the outlet of the reactor when the test was performed at 400 °C, while it reached 50 °C for tests conducted at 500 °C.

These thermal profiles were considered as unacceptable for the control of the reactor operating conditions, thus some improvements were adopted. The modification of the high temperature zone consisted in replacing the preheater ceramic heater with another one longer, which allowed to uniformly irradiating also the mixing zone. Subsequent thermal tests showed a modification of the temperature profile into a flat one even at high temperatures.

Non–catalysed gasification tests were carried out with some biomass model compounds as feedstock. In particular, glycerol was adopted as the model compound of the lipid fraction, while glucose was used as representative of carbohydrates. In figure 5.5, the most representative tests are reported.

In the tests with glucose (test n.1 and 2), a gasification efficiency of 18.1 and of 41.6% was obtained when the operating temperature was 450 and 500 °C, respectively. Although the residence time in the test at 450 °C was higher, the mass of obtained gas was much lower than with the test at 500 °C: an increase of just 50 °C could significantly affect the overall performance of the process. In both tests a high concentration of hydrogen (around 50%) and carbon dioxide (37-30%) followed by carbon monoxide (13-16%) was found in the gas phase. Light hydrocarbons such as methane, ethane and ethylene were found in very small amounts.

The test with glycerol were carried at temperature of 488 °C and pressure of 26 MPa. Comparing the test conducted at the same residence time (9 seconds, tests n.3 and 4) but different initial concentration a difference in the gasification efficiency and composition of the gas phase was obtained.

In particular, it is increasing in concentration of glycerol in the reactor from 2% w / w to 12.5% w / w of the gasification efficiency decreases by 7.9% to 3.4%.

Some authors explain this result, assuming that the pyrolysis reactions and steam reforming of glycerol occur simultaneously. The steam reforming reaction requires the presence of water to take place while the pyrolysis reaction occurs even in the absence of water. The decomposition of a generic model compound for the steam reforming (eq. 1) and pyrolysis (eq. 2) is represented below [25, 26]:

$$CH_xO_y + (2-y) * H_2O \rightarrow CO_2 + \left(2 + \frac{x}{2} - y\right) * H_2 \qquad \text{(eq. 1)}$$

$$CH_xO_y \rightarrow Gas\ products\ (H_2, CO, CO_2, CH_4, and\ other\ hydrocarbons) +$$
$$Liquid\ products\ (aldehydes, ketones, alcohols, carboxylic\ acids) + Char \qquad \text{(eq. 2)}$$

Since water is a reactant for the steam reforming reaction, its concentration may influence the reaction. The pyrolysis reaction, however, is insensitive to the concentration of water. For very high concentrations of glycerol, water it may even become the limiting reagent and the pyrolysis reaction become the main source of gas production. The high concentration of biomass in the reactor inhibits the steam reforming reaction and consequently the gasification decreases. At high biomass concentrations in the reactor the gas composition changes: it becomes richer in CO (from 12.3% to

27.4%) and methane (from 0.8% to 2.5%). The concentration of hydrogen in the gases produced instead, it decreases from 51.8% to 33.1%. These results also confirm that pyrolysis is the main route of reaction since the percentage of CO and light hydrocarbons have increased greatly [25].

Another comparison can be made between two tests with glycerol in which the treatment time was 18.1 and 5.5 seconds, respectively, while all other parameters were the same (test n. 5 and n. 6). The high treatment time corresponded to a gasification efficiency (20.8%) much higher than that of the other test (1.3%). It should be noted that in both tests the concentration of hydrogen are high (52.2 and 56.9%). Increasing the residence time from 5.5 sec to 18.1 sec the CO concentration decreases from 26.1% to 13.3% while the CO_2 concentration increases from 13.2% to 31.0%. This result can be explained assuming that the reaction of water gas shift takes place at high reaction times and manages to convert CO into CO_2 by varying the composition of the mixture.

For the experiments shown in figure 5.5, the carbon mass balance was 80% for the test with high gasification efficiency and 96% for the test with low GE. These results suggest that the adopted sampling and analytical procedures are reliable. In fact, at low conversions, the reaction produces negligible amount of solid products and 96% of the initial carbon was recovered only in the liquid and gas phases. For the experiments at high conversion, in which large amounts of gas was obtained, it could be hypothesised that about 20% of the fed carbon was transformed into not collected solid products.

Model compound	**T [°C]**	**P [bar]**	**Concentration in the reactor [wt.%]**	**Time [sec]**	**Reynolds number**	**Balance sheet of carbon atoms [wt.%]**	**Mass of gas / mass of fed compound (GE)**	**Gas composition**					
								%mol H2	**%mol CO**	**%mol CH4**	**%mol CO_2**	**%mol C_2H_4**	**%mol C_2H_6**
Glucose	450	260	0.8%	19.2	400	88.8%	18.1%	46.3%	16.0%	0.5%	36.9%	0.2%	0.1%
Glucose	500	260	0.8%	15.7	380	80.4%	41.6%	53.3%	13.4%	2.5%	29.9%	0.5%	0.4%
Glycerol	488	260	12.5%	9.0	665	96.0%	3.4%	33.1%	27.4%	2.5%	34.4%	2.1%	0.4%
Glycerol	488	260	2.0%	9.0	665	89.4%	7.9%	51.8%	12.3%	0.8%	34.3%	0.7%	0.2%
Glycerol	488	260	2.0%	18.1	330	82.5%	20.8%	52.2%	13.3%	1.6%	31.0%	1.4%	0.5%
Glycerol	488	260	2.0%	5.5	725	95.9%	1.3%	56.9%	26.1%	2.4%	13.2%	1.2%	0.3%

Figure 5.5. Gasification tests results of model compounds in supercritical water

In figure 5.5 the Reynolds number (Re) is also shown for each experiments. Very few studies are reported in literature on the influence of this process parameter, related to the flow regime, on hydrothermal conversion process. However, it seems to have a certain influence on the gasification yields, as reported by D. Hendry and co-workers [27]. They have carried out experiments of gasification of alcohols and have shown that when the gasification reaction is conducted at turbulent regime, the gasification rate is much higher than in laminar flux. In Figure 5.6 the relationship between the fluid-dynamic regime (Reynolds number) and the gasification rate. The y-axis on the right shows the corresponding gasification efficiency (GE).

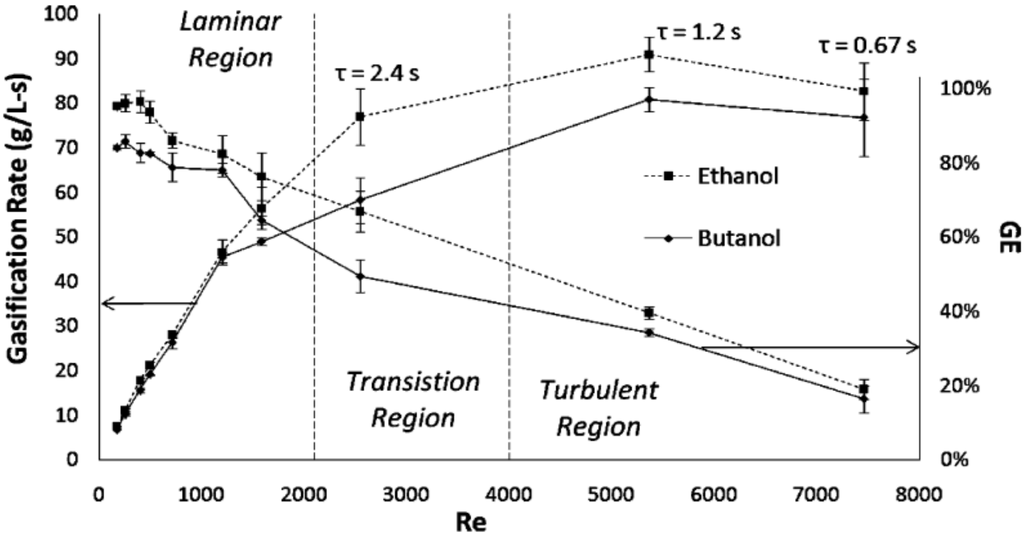


Figure 5.6. Relationship of Reynolds number and gasification of alcohols [27].

The authors calculated the gasification rate as follows:

$$Gasification\, rate = \frac{c}{\tau} * (\%GE)$$

where *c* (g/L) represents the mass concentration of the reactant at the reactor inlet, τ (s) is the residence time and *GE* (%) the gasification efficiency. This parameter defined with such an expression could be assumed as the variation of the feed concentration in the reactor divided by the average residence time.

In the laminar region Re < 2000 an increase in the Reynolds number, produces a significant increase in the gasification rate (the dependence is linear). In the transition region (2000 < Re < 4000) the Reynolds number increase continues to enhance the speed of gasification but the effect is less strong. The developed turbulent regime is the best fluid dynamic condition for the gasification reactions [28]. Turbulent flow, increases axial mixing, eliminating axial temperature and concentration gradients [27]. It must be noted that for Reynolds values greater than 5000 the dependence of gasification on the fluid-dynamic regime appears to be extinguished. Thus, it is no longer useful for the process and, hence, convenient to further increase the Reynolds number, since the reactions are not enhanced, while pressure drop increase and cause higher the costs of management. Increasing the flow in fact the pressure drop increase, consequently the pumping costs impact on the economy of the process.

The experiments showed in the figures have all been carried out in laminar flow regime.

In general, in order to vary the hydrodinamic regime without changing the reactor residence time the only possible options are to vary the inner geometry of the reactor either to insert turbulence promoters.

For the lab-scale experimental setup descrivbed above, the reactor inner volume was reduced by inserting small glass spheres. The bed of spheres occupied about 59% of the total reactor volume; the calculation of the Reynolds number for the new reactor layout was performed with the following formula [29, 30]:

$$Re_p = \frac{\rho * v * D_p}{\mu * (1 - \epsilon)}$$

Where ρ and μ are the density and the dynamic viscosity of the fluid, respectively; D_p is the mean diameter of the spheres, v is the velocity that the fluid would have inside the reactor in the absence of the spheres, and ε is the degree of vacuum (about 41%).

A comparison between two tests under the same operating conditions but different fluid dynamic conditions is shown in figure 5.7. By entering the fixed bed of spheres the Reynolds number increased from 442 to 665 and the gasification efficiency increased from 2.6 to 7.9%. Even if the variation of the Reynolds number is very small, a significant increase of the gaseous products was obtained. This result is in agreement with the strong dependancy of the gasification rate on the fluid dynamics, especially in the laminar region, as above reported.

Model compound	**T [°C]**	**P [bar]**	**Concentration in the reactor [wt.%]**	**Time [sec]**	**Reynolds number**	**Balance sheet of carbon atoms [wt.%]**	**Mass of gas / mass of fed compound (GE)**	**Gas composition**					
								%mol H2	**%mol CO**	**%mol CH4**	**%mol CO2**	**%mol C2H4**	**%mol C2H6**
Glycerol	488	260	2.0%	9.0	665	89.4%	7.9%	51.8%	12.3%	0.8%	34.3%	0.7%	0.2%
Glycerol	488	260	2.0%	9.0	442	95.5%	2.6%	50.3%	28.9%	4.6%	13.1%	2.5%	0.6%

Figure 5.7. Gasification tests results of glycerol in supercritical water at different fluid dynamics regime.

Decreasing the Reynolds number the concentration of H_2 remain virtually constant, the concentration of CO_2 decrease a lot, the concentration of CO and light hydrocarbons significantly increases. These results can be explained similarly as done to study the effect of the concentration of dry biomass on gasification. Even in this case, in fact, the steam reforming reaction (eq. 1) and the pyrolysis reaction (eq. 2) occur simultaneously. It is reasonable to assume that the steam reforming reaction is favoured when there is no concentration gradients, and the mass transfer coefficient is high. The pyrolysis reaction however, can also occur at high concentration gradients and when the coefficient of mass transfer is low.

By increasing the Reynolds number, the axial mixing increases, and the resistance to mass transfer it decreases. Consequently, the steam reforming reaction is favoured for high Reynolds number, the lower the Reynolds number of the pyrolysis reaction is the favoured reaction.

The presence of the spheres really, influences the fluid-dynamic regime since it varies the motion of the fluid through the packed bed. The fluid in fact varies the direction of motion through the bed of spheres and this increases the transport coefficients. The Reynolds number is defined as the ratio between the inertial forces and viscous forces acting on the fluid. The inertial forces of a fluid flowing through a tube containing the inserts is higher than the case in which the tube is empty, while the viscous forces remain unchanged. Consequently, the two systems (reactor with spheres and without spheres) represent a bit different configurations and can be compared only qualitatively.

The results reported as comparison between the two different configurations have the aim of highlighting the dependence of gasification from the fluid-dynamic regime.

5.12 Adaptation to treat real biomass

The continuous system was implemented to move the algal biomass in aqueous suspension. The piston pumps are suitable for handling clean liquids, therefore the presence of dust or fine suspension in the feed tank cause a malfunction of the pump (leakage in the piston gasket, fouling/clogging of the check valve, etc.). For the biomass in suspension was therefore necessary to adopt a specific-purpose high-pressure syringe pump constituted by a movable piston inserted into a cylinder.

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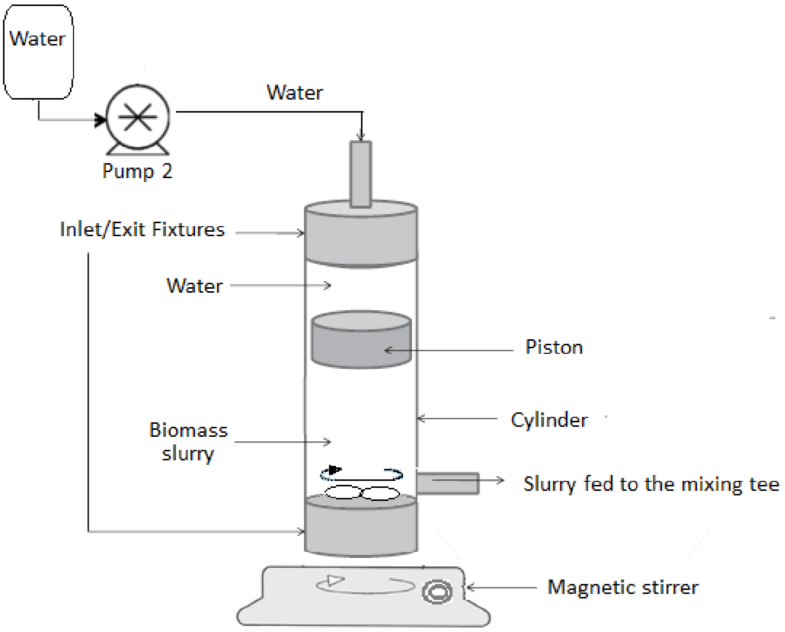


Figure 5.8. A schematic of the syringe pump used to feed algal biomass into a continuous plant [28].

To maintain a homogeneous suspension during the entire duration of the tests, a stirring system has been provided with the use of a magnetic stir bar inside the cylinder at the bottom of the feedstock side; a magnetic plate located out from the cylinder drove the stirring bar. To carry out a test is necessary to previously load the cylinder with the suspension to feed.

The Figure 5.9 shows the flow sheet continuous plant with the enabled device for the handling of algal suspension at high pressures.

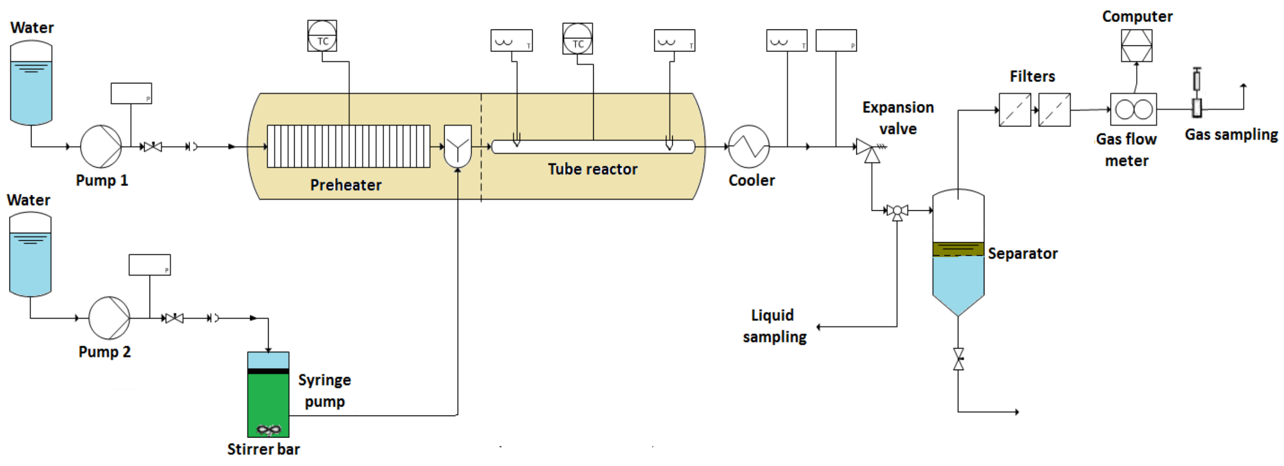


Figure 5.9. Flow sheet of the plant in continuous laboratory scale developed for the treatment of algal biomass in supercritical water.

5.13 Conclusions and future developments

In this chapter, the development of a continuous reaction system for hydrothermal conversion of biomass and model compounds was presented.

Some preliminary tests of non-catalytic SCWG of glycerol and glucose as biomass model compounds were performed and the obtained results were reported with a discussion on the influence of the most important process parameters.

The layout of the reactor was chosen to possibly study the gasification process also in the presence of heterogeneous catalysts. A future work will be the use of a fixed bed of a suitable catalyst for gasification experiment. In addition, hydrothermal conversion of triglycerides rather than water-soluble model compounds will be carried out, with also the intent of to making a comparison with the results obtained in batch mode and reported in the previous chapter.

Further work will also deal with the modification of the reactor geometry in order to perform test in a larger range of Reynolds number to assess the influence of such a parameter, also possibly not varying the residence time inside the reactor.

REFERENCE

[1] A. Kruse, N. Dahmen. Water – A magic solvent for biomass conversion, J. of Supercritical Fluids 96 (2015) 36–45.

[2] N. Dahmen, E. Henrich, A. Kruse, K. Raffelt, Biomass Liquefaction and Gasification, in: Biomass to Biofuels: Strategies for Global Industries, 2010, pp.89.

[3] P. Azadi, R. Farnood, Review of heterogeneous catalysts for sub- and supercritical water gasification of biomass and wastes international journal of hydrogen energy 36 (2011) 9529e9541.

[4] Osada M, Sato T, Watanabe M, Shirai M, Arai K. Catalytic gasification of wood biomass in subcritical and supercritical water. Combust Sci. Technol. (2006), 178:537e52.

[5] Davda RR, Dumesic JA. Renewable hydrogen by aqueous phase reforming of glucose. Chem. Commun; (2004):36e7.

[6] Xu X, Matsumura Y, Stenberg J, Antal MJ. Carbon-catalyzed gasification of organic feedstocks in supercritical water. Ind. Eng. Chem. (1996), 35:2522e30.

[7] Huber GW, Shabaker JW, Dumesic JA. Raney Ni-Sn catalyst for H2 production from biomass-derived hydrocarbon. Science (2003), 300:2075e7.

[8] Elliott DC, Sealock LJ, Baker EG. Chemical processing in high-pressure aqueous environments. 2. Development of catalysts for gasification. Ind. Eng. Chem. (1993), 32:1542e8.

[9] Yamamura T, Mori T, Park KC, Fujii Y, Tomiyasu H. Ruthenium(IV) dioxide-catalyzed reductive gasification of intractable biomass including cellulose, heterocyclic compounds, and sludge in supercritical water. J Supercrit. Fluids (2009), 51:43e9.

[10] Resende FLP, Savage PE. Effect of metals on supercritical water gasification of cellulose and lignin. Ind. Eng. Chem. (2010), 49:2694e700.

[11] Shabaker JW, Huber GW, Davda RR, Cortright RD, Dumesic JA. Aqueous-phase reforming of ethylene glycol over supported platinum catalysts. Catal. Lett. (2003) 88:1e8.

[12] Nishimura S. Handbook of heterogeneous catalytic hydrogenation for organic synthesis. 1st ed. NJ: John Wiley and Sons; 2001.

[13] Ertl G, Knozinger H, Weitkamp J. Preparation of solid catalysts. 1st ed. Wiley-VCH; 1999.

[14] Azadi P, Syed KM, Farnood R. Catalytic gasification of biomass model compound in near-critical water. Appl. Catal. A. (2009), 358:65e72.

[15] Smith HA, Bedoit WC, Fuzek JF. The preparation and aging of Raney nickel catalysts. J. Am. Chem. Soc. (1949), 71:3769e71.

[16] Lu Y, Li S, Guo L, Zhang X. Hydrogen production by biomass gasification in supercritical water over Ni/ϒ-Al2O3 and Ni/CeO2-ϒ-Al2O3 catalysts. Int. J. Hydrogen Energy (2010), 35:7161-8.

[17] Waldner MH, Krumeich F, Vogel F. Synthetic natural gas by hydrothermal gasification of biomass selection procedure towards a stable catalyst and its sodium sulfate tolerance. J. Supercrit. Fluids (2007), 43:91e105.

[18] Azadi P, Khodadadi AA, Mortazavi Y, Farnood R. Hydrothermal gasification of glucose using Raney nickel and homogeneous organometallic catalysts. Fuel Process Technol. (2009), 90:145-51.

[19] Zhang R, Jiang W, Cheng L, Sun B, Sun D, Bi J. Hydrogen production from lignite via supercritical water in flow-type reactor. Int. J. Hydrogen Energy (2010), 35:11810e5.

[20] Watanabe M, Inomata H, Arai K. Catalytic hydrogen generation from biomass (glucose and cellulose) with ZrO2 in supercritical water. Biomass & Bioenergy (2002), 22:405e10.

[21] Lu YJ, Guo LJ, Ji CM, Zhang XM, Hao XH, Yan QH. Hydrogen production by biomass gasification in supercritical water: a parametric study. Int. J. Hydrogen Energy (2006), 31:822e31.

[22] Yanik J, Ebale S, Kruse A, Saglam M, Yuksel M. Biomass gasification in supercritical water: II. Effect of catalyst. Int. J. Hydrogen Energy. (2008) 33:4520-6.

[23] Matsumura Y, Minowa T. Fundamental design of a continuous biomass gasification process using a supercritical water fluidized bed. Int. J. Hydrogen Energy (2003), 29:701e7.

[24] Potic B, Kersten SRA, Ye M, Van der Hoef MA, Kuipers JAM, Van Swaaij WPM. Fluidization with hot compressed water in micro-reactors. Chem. Eng. Sci. (2005), 60:5982e90.

[25] S. Guo, L. Guo, C. Cao, J. Yin, Y. Lu, X. Zhang. Hydrogen production from glycerol by supercritical water gasification in a continuous flow tubular reactor. International journal of hydrogen energy (2012), 37:5559-5568.

[26] T. Valliyappan, N.N. Bakhshi, A.K. Dalai. Pyrolysis of glycerol for the production of hydrogen or syn gas. Bioresource Technology. (2008), 99:4476–4483.

[27] D. Hendry, A. Miller, W. Jacoby. Turbulent Operation of a Continuous Reactor for Gasification of Alcohols in Supercritical Water. Ind. Eng. Chem. Res. (2012), 51:2578−2585.

[28] A. Miller, D. Hendry, N. Wilkinson, C. Venkitasamy, W. Jacoby. Exploration of the gasification of Spirulina algae in supercritical water. Bioresource Technology. (2012), 119:41–47.

[29] W.E. McCabe, J.C. Smith, and P.Harriott (2001). Unit Operations of Chemical Engineering, McGraw Hill, New York.

[30] Perry's Chemical Engineers Handbook, 7-th Edition. (1997). Ed: R.H. Perry, D.W. Green, and J.O. Maloney), McGraw-Hill, New York.

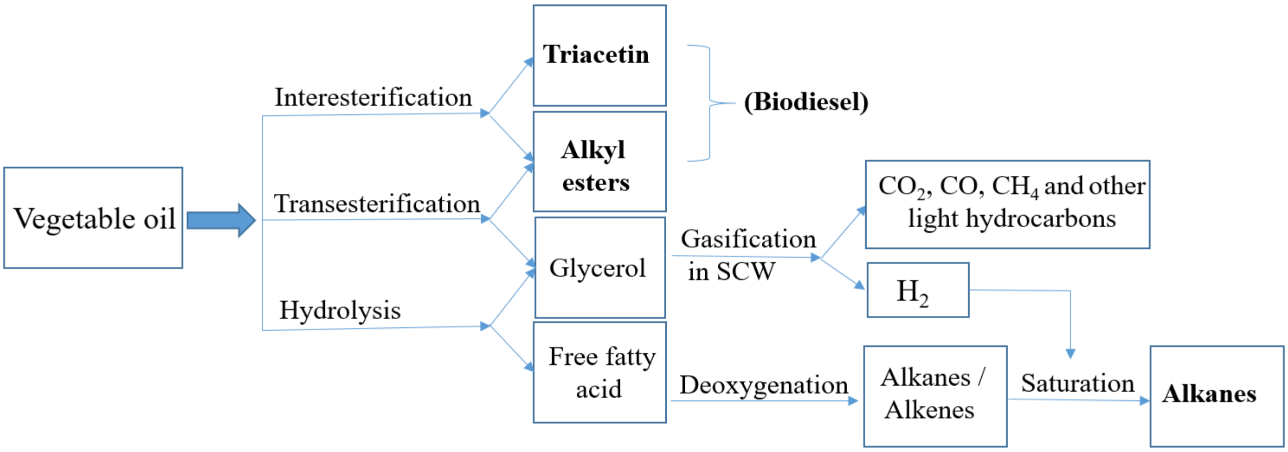
SUMMARY AND GENERAL CONCLUSIONS

Aim of this work was to study the conversion of triglycerides into biofuels with heterogeneous catalysts, and at the same time, the exploitation of glycerol obtained as a co-product in some of the possible transformation paths. The conversion of triglycerides was performed through two main routes: the production of biodiesel and the production of hydrocarbons.

For what regards the production of biodiesel two synthetic routes were studied i.e. the transesterification and interesterification using heterogeneous acid catalysts. Tin (II) oxide has provided excellent catalytic performances for both processes and therefore can be considered an interesting heterogeneous catalyst for the production of biodiesel. The interesterification process has been studied since it represents an innovative process with several advantages including the production of triacetin in place of glycerol, which has been shown in the literature to be a good additive for the final biodiesel mixture.

The other route of triglycerides transformation was hydrothermal deoxygenation of free fatty acids without the addition of external hydrogen, in order to obtain linear hydrocarbons. The hydrothermal treatment makes possible in a first stage, the hydrolysis of triglycerides into fatty acids and glycerol but it can be also used to carry out the reaction of deoxygenation. The water in fact plays a key role in these processes thanks to its special properties when it reaches the supercritical condition. Among the benefits of water utilization it must be considered its potential ability to provide hydrogen when reforming reactions take place. Particular attention was paid to the gasification of glycerol, as it can be an important method for the production of molecular hydrogen that can be used for the saturation of the double bonds present in the fatty acid chain.

The figure below schematically summarizes the possible ways of vegetable oil conversion studied in this work. It must be noticed that in this way the oil can be transformed with an integrated process in which the advantages of a method of conversion can compensate for the weaknesses of the other, and that the co-products are minimized.



The diagram shows an integrated process in which different techniques can be used in order to maximize the conversion of vegetable oil into biofuels.

All of these reactions require catalysts to take place in mild conditions and in a short time. Heterogeneous catalysts mainly based on nickel have been tested for the deoxygenation of stearic acid in the absence of hydrogen and for the gasification of glycerol. Interesting results have been obtained in this thesis with Raney nickel which showed interesting catalytic activity both for the production of linear hydrocarbons from stearic acid and for the gasification of glycerol. High yields in products of interest were achieved even if the operating conditions have yet to be optimized. For this purpose it was assembled and presented a continuous flow reaction system and selected gasification tests of glycerol in supercritical water were carried out in it. It has been shown that low residence times and high temperatures represent the best operating conditions to obtain high yields of hydrogen. In addition, beneficial effects on the performance of the process are associated to low initial concentration of the reactant and high Reynolds number in the reactor. The fluid dynamic regime in particular, deserves further study, given the limited information that can be found in the literature and that was collected in this study.