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Development of a low pressure, catalytic process for the production of biofuels

DISSERTATION

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STATUTORY DECLARATION

I declare that I have authored this thesis independently, that I have not used other than the declared sources / resources and that I have explicitly marked all material which has been quoted either literally or by content from the used sources.

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Abstract

The need for low fuel prices, energy independence of countries and mitigation of global warming had as a result the development of biofuel production technologies. The EU has set as a reference target a 5.75% market share for biofuels in 2010. The thermochemical conversion technologies have been attracting scientific attention, since they can convert a wide variety of biogenic raw materials into liquid biofuels with desirable properties. The addition of catalysts into the conversion system has a result the production of biofuels with improved characteristics.

The development of a Catalytic Low Pressure Liquefaction process (in german Katalytische Niederdruck Verölung – KNV) for the production of biofuels was presented. Low pressure conversion can give the possibility to better regulate the residence time of produced vapours into the reactor system, enabling the increase of liquid product yield without the use of high-investment reactors. The zeolite addition can improve the quality of the liquid product. The yields, the chemical composition, the elemental composition and the physical properties of the conversion products were presented after each test.

The co-conversion of rapeseed cake and safflower oil was examined, in the absence of catalysts and in the presence of three different zeolite catalysts (Fe-ZSM-5, H-ZSM-5 and H-Beta) at 400 ℃ and 350 ℃. The rapeseed cake conversion with two reactor configurations (with or without a vapour upgrading section) was examined in the absence of catalysts and in the presence of two different zeolite catalysts (H-ZSM-5 and H-Beta) at 400 ℃. The separate conversion of meat meal C1 and algae was examined in the presence of the H-ZSM-5 zeolite at 400 ℃, without and with a vapour upgrading section, respectively. The energy balance of the different conversion tests at 400 ℃ was calculated and evaluated.

The feasibility study for the upscaling of the KNV laboratory process into a pilot plant, using algae as a feedstock, was performed. Two Design Layouts were employed: (A) using a gas burner to heat up the reactor and (B) using an induction generator to heat up the reactor. The fixed investment costs, the labour costs, the energy and auxiliary material costs as well as the production costs were assessed. The payback time for each Design Layout was calculated. Both feasibility studies were evaluated.

Keywords

zeolite catalysts; low pressure conversion; co-conversion; rapeseed cake; vegetable oil; biogenic waste; vapour upgrading; biofuel

Kurzfassung

Die Notwendigkeit niedriger Treibstoffpreise, Energie - Unabhängigkeit und Reduktion der Erderwärmung resultierte in der Entwicklung von Produktionstechnologien für Bio-Treibstoffe. Die EU hat als Ziel bis 2010 einen Marktanteil von 5,7% des Gesamttreibstoffbedarfes an biogenen Treibstoffe definiert. Thermochemische Konversionstechnologien zogen die Aufmerksamkeit von Wissenschaftlern an, da sie eine große Vielzahl an nachwachsenden Rohstoffen zu flüssigen Treibstoffen umsetzen können, bei Einhaltung der erwünschten Eigenschaften. Durch das Verwenden von Katalysatoren im Konversionsprozess wurden Biotreibstoffe mit verbesserten Eigenschaften erhalten.

In der vorliegenden Arbeit wird die Entwicklung einer Katalytischen Niederdruck Verölung KNV für die Produktion von Bio-Treibstoffen vorgestellt. Niederdruck Verölung kann eine bessere Regulierung der Verweilzeit von produzierten Dämpfen im Reaktorsystem ermöglichen. Dies ermöglicht eine Erhöhung der Reaktorausbeute an Flüssigprodukt, ohne dass hochpreisige Reaktoren eingesetzt werden müssten. Die Beigabe von Zeolit kann die Qualität des Flüssigproduktes verbessern. Zu jedem Versuch werden die Erträge, chemische Zusammensetzung, atomare Zusammensetzung und physikalische Eigenschaften dargestellt.

In der Arbeit wurde die geichzeitige Umwandlung von Rapspress-Kuchen und Distelöl untersucht, wobei einmal keine Katalysatoren, in anderen Versuchen drei verschiedene Zeolith-Katalysatoren (Fe-ZSM-5, H-ZSM-5 und H-Beta) bei 400 ℃ und 350 ℃ eingesetzt wurden. Die Umwandlung von Rapspress-Kuchen bei zwei verschiedenen Reaktor Konfigurationen (mit oder ohne Dampf Reinigung) wurde einmal ohne Katalysatoren und die anderen Male in Anwesenheit von zwei verschiedenen Zeolith Katalysatoren (H-ZSM-5 und H-Beta) bei 400 ℃ untersucht. In getrennten Versuchen wurden Tiermehl C1 und Algen in Anwesenheit von H-ZSM-5 Zeolith bei 400 °C untersucht, sowohl mit als auch ohne Dampf Reinigung. Die Energiebilanz der verschiedenen Umwandlungsversuche bei 400 °C wurde berechnet und evaluiert.

Es wurde eine Feasibility-Studie für das Upscaling einer Katalytischen Niederdruck Verölung KNV vom Labourmaßstab zum Pilot-Plant-Maßstab, unter Verwendung von Algen als Rohmaterial durchgeführt. Hier wurden zwei Anlagen-Ausführungen verglichen: (A) ein Gasbrenner zur Erhitzung des Reaktors, (B) ein Induktionsheizgerät zur Erhitzung des Reaktors. Ebenso wurden die Fixkosten für die Anlagen-Investition, Personalkosten, kosten für Energie und Hilfsstoffe und Produktionskosten abgeschätzt. Die Amortisaitonszeit für jede Anlagen-Ausführung wurde berechnet. Danach wurden beide Feasibility Studien verglichen.

Schlagwörter

Zeolit Katalysatoren; Niederdruck Konversion; Co-Konversion; Rapskuchen; pflanzliches Öl; Biomüll; Dampfraffination; Biotreibstoff

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Kanellina Giannakopoulou,

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1 INTRODUCTION

1.1 BIOFUELS OVERVIEW

1.1.1 THE ENERGY SECTOR TODAY

For the past decades the energy sector has been facing some major problems.

During the period 2001-2005 the oil dollar price tripled. Although the exchange rate movements cushioned the effect, Europe saw oil prices more than double. Over the next twenty to thirty years, the European Union (EU) fossil oil production is expected to decline, while the transport demand is likely to continue to grow. The world oil demand is also expected to show strong growth. The global distribution of the known fossil oil reserves will leave the Middle East Organization of Petroleum Exporting Countries (OPEC) members, as the main suppliers for this increased demand, although the accelerated exploitation of Canadian and Venezuelan tar sands could provide up to 3% of the world fossil oil production by 2010 (Commission of the European Communities, 2006a).

The still available crude oil resources amount cannot be easily estimated, but it is believed to be gradually decreasing. Countries have been seeking to their energy independence for economic and political reasons. The environmental effect of the greenhouse gases is profound today, due to the presence of the extreme meteorological phenomena that take place around the globe.

In EU-27, almost 1/3 of the final energy was consumed in the transportation sector in the year 2005 (Directorate General for Energy and Transport, 2008).

Because of its almost complete dependency on fossil oil, transportation accounts for more than half the fossil oil used in the EU and this share is increasing. The growing demand in the transportation sector is the main reason for the growth in the overall EU oil consumption (Commission of the European Communities, 2006a).

In EU-27, transportation was responsible for an estimated 23.4% of all greenhouse gas emissions that are contributing to global warming. Between 1990 and 2003, when greenhouse gas emissions in the EU saw an overall reduction, the transportation share grew by about 24%. The reduction of the greenhouse gas emissions from transportation, therefore, could contribute significantly to meeting the EU Kyoto targets (Commission of the European Communities, 2006a).

Plants are abundant biogenic resources that use light, nutrients and CO_2 for their growth and multiplication. Their exploitation for the production of biofuels would have as a result the creation of a carbon cycle, where the produced CO_2 emissions would be re-captured and be used for the growth of new plants. The emissions level could be initially stabilized, while CO_2 mitigation could be finally achieved.

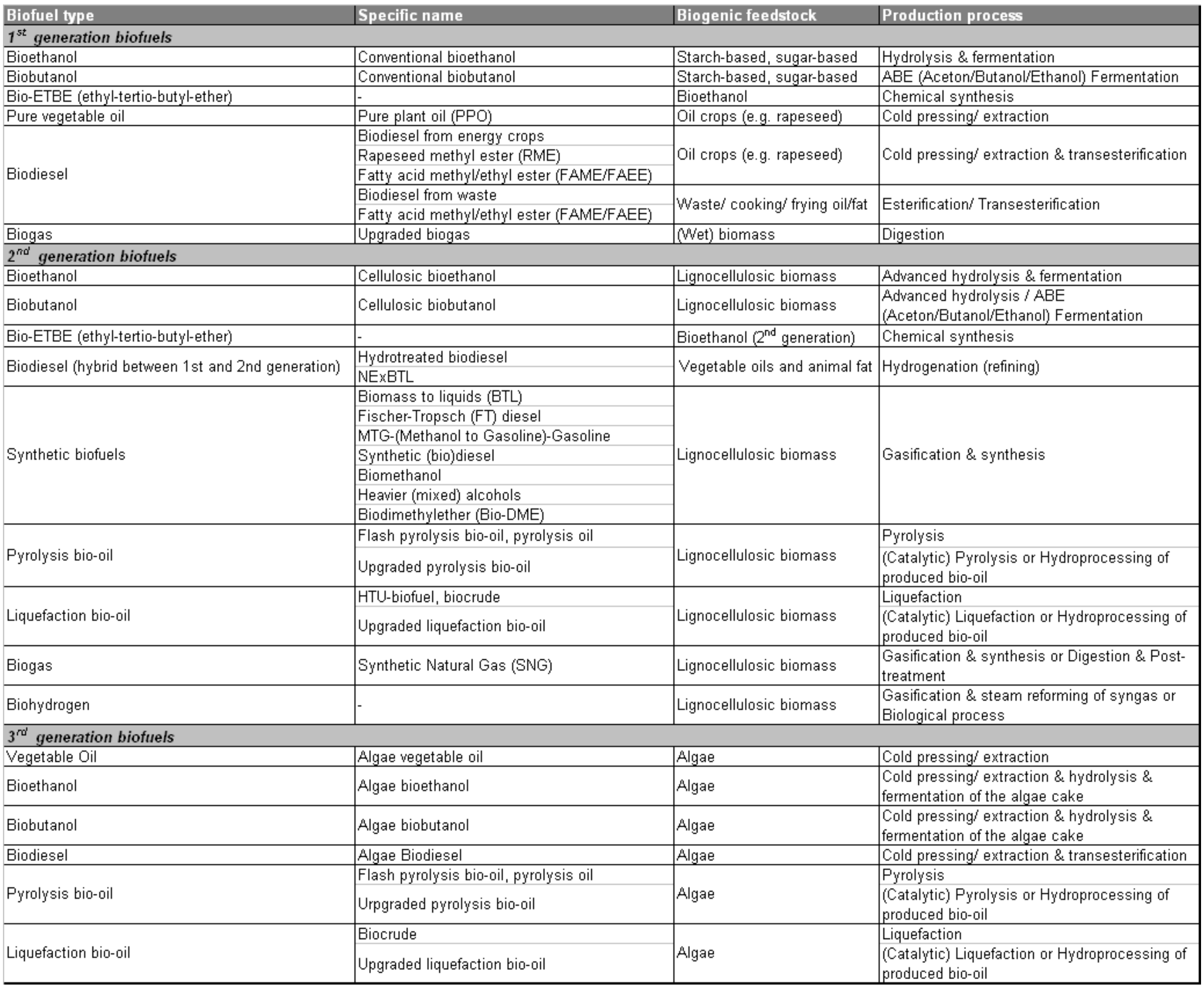
Apart from fossil based liquified petroleum gas (LPG) and compressed natural gas (CNG), liquid biofuels are currently one of the few possible substitutes for fossil oil based transportation fuel. They can easily be put on the market now and provide immediate greenhouse gas reductions. In contrast to fossil oil reserves, which are concentrated in a relatively small number of geographical regions, the raw material for biofuels can be produced nearly anywhere on earth. Thus, increasing the share of biofuels in EU transportation fuels could help to broaden the range of the EU energy suppliers (Commission of the European Communities, 2006a).

In the EU transportation sector, fossil oil is the main energy source with a 98% contribution to all transportation fuels. In 2002, alternative motor fuels contributed 2% and biofuels only 0.3%. However, during the last years the contribution of biofuels has increased due to the implementation of the biofuels directive in several Member States (Commission of the European Communities, 2006a).

1.1.2 BIOFUEL GENERATIONS

Biofuels can be classified according to the feedstock used during their production process. The following Table presents the different biofuel generations and the main biofuel types produced:

Table 1-1: Biofuel classification into generations according to the used biogenic feedstock



Biofuel type	Specific name	Biogenic feedstock	Production process
1st generation biofuels			
Bioethanol	Conventional bioethanol	Starch-based, sugar-based	Hydrolysis & fermentation
Biobutanol	Conventional biobutanol	Starch-based, sugar-based	ABE (Aceton/Butanol/Ethanol) Fermentation
Bio-ETBE (ethyl-tertio-butyl-ether)	-	Bioethanol	Chemical synthesis
Pure vegetable oil	Pure plant oil (PPO)	Oil crops (e.g. rapeseed)	Cold pressing/ extraction
Biodiesel	Biodiesel from energy crops Rapeseed methyl ester (RME) Fatty acid methyl/ethyl ester (FAME/FAEE)	Oil crops (e.g. rapeseed)	Cold pressing/ extraction & transesterification
	Biodiesel from waste Fatty acid methyl/ethyl ester (FAME/FAEE)	Waste/ cooking/ frying oil/fat	Esterification/ Transesterification
Biogas	Upgraded biogas	(Wet) biomass	Digestion
2nd generation biofuels			
Bioethanol	Cellulosic bioethanol	Lignocellulosic biomass	Advanced hydrolysis & fermentation
Biobutanol	Cellulosic biobutanol	Lignocellulosic biomass	Advanced hydrolysis / ABE (Aceton/Butanol/Ethanol) Fermentation
Bio-ETBE (ethyl-tertio-butyl-ether)	-	Bioethanol (2nd generation)	Chemical synthesis
Biodiesel (hybrid between 1st and 2nd generation)	Hydrotreated biodiesel NExBTL	Vegetable oils and animal fat	Hydrogenation (refining)
Synthetic biofuels	Biomass to liquids (BTL) Fischer-Tropsch (FT) diesel MTG-(Methanol to Gasoline)-Gasoline Synthetic (bio)diesel Biomethanol Heavier (mixed) alcohols Biodimethylether (Bio-DME)	Lignocellulosic biomass	Gasification & synthesis
Pyrolysis bio-oil	Flash pyrolysis bio-oil, pyrolysis oil	Lignocellulosic biomass	Pyrolysis
	Upgraded pyrolysis bio-oil		(Catalytic) Pyrolysis or Hydroprocessing of produced bio-oil
Liquefaction bio-oil	HTU-biofuel, biocrude	Lignocellulosic biomass	Liquefaction
	Upgraded liquefaction bio-oil		(Catalytic) Liquefaction or Hydroprocessing of produced bio-oil
Biogas	Synthetic Natural Gas (SNG)	Lignocellulosic biomass	Gasification & synthesis or Digestion & Post-treatment
Biohydrogen	-	Lignocellulosic biomass	Gasification & steam reforming of syngas or Biological process
3rd generation biofuels			
Vegetable Oil	Algae vegetable oil	Algae	Cold pressing/ extraction
Bioethanol	Algae bioethanol	Algae	Cold pressing/ extraction & hydrolysis & fermentation of the algae cake
Biobutanol	Algae biobutanol	Algae	Cold pressing/ extraction & hydrolysis & fermentation of the algae cake
Biodiesel	Algae Biodiesel	Algae	Cold pressing/ extraction & transesterification
Pyrolysis bio-oil	Flash pyrolysis bio-oil, pyrolysis oil	Algae	Pyrolysis
	Urpgraded pyrolysis bio-oil		(Catalytic) Pyrolysis or Hydroprocessing of produced bio-oil
Liquefaction bio-oil	Biocrude	Algae	Liquefaction
	Upgraded liquefaction bio-oil		(Catalytic) Liquefaction or Hydroprocessing of produced bio-oil

The 1st generation biofuels have been exploiting feedstocks which are edible for humans, containing oils, fats, starch and sugar. The most widely produced biofuels of this generation are bioethanol and biodiesel. They have been used as transportation fuels either alone or in blends with conventional fuels. Several bioethanol and biodiesel commercial production plants have been operating around the world. The EU has supported the scientific research in this area and the penetration of these fuels into the market. Still, the use of these feedstocks have deprived humans of materials with high nutrient value, bringing up economic and moral issues on the biofuel market.

The idea of producing biofuels from lignocellulosic materials appeared to provide a solution to the mentioned problem. As a result, the 2nd generation biofuels emerged. Due to the more complex chemical structure of these feedstocks, different conversion processes had to be developed. Increased scientific research, with the support of the EU, has managed to develop new processes for the conversion of lignocellulosic materials into biofuels that could be used in engines, turbines or boilers. These conversion processes are still facing some challenges. Therefore the penetration of the 2nd generation biofuels into the fuel market is limited for the moment.

Studies on biofuel strategies have shown that the key factors for the establishment of a bio-based energy economy is (a) the availability of arable land for biomass cultivation and (b) the productivity rates of different biomass types. The 3rd generation biofuels emerged by the idea to use algae as feedstock, since they demonstrate high productivity rates and no demand in arable land for their cultivation. On a more general approach, the 3rd generation biofuels were defined by the use of specially designed/engineered energy crops that would allow an improved conversion. With the help of biotechnology, plant characteristics could be altered in a positive way, so that plants with e.g. higher oil/sugar/starch content, lower lignin content, ability to grow on acidic soil or higher productivity could be produced. In this case, the produced biofuel types would again be bioethanol, biodiesel, synthetic fuels, pyrolysis bio-oils, e.t.c. This generation is in the early stages of development and mainly uses the 2nd generation conversion techniques.

Finally, the new idea of developing the 4th generation biofuels has started to grow. As feedstock, tailor-made plants will be used with enhanced carbon storage ability. This carbon-rich biomass would then be converted to biofuel using the 2nd generation conversion technologies. The produced emissions from the conversion process will be captured and then geo-sequestered in suitable fields, where they could be stored for hundreds or thousands of years. It is soon to predict how this biofuel generation will evolve, but it has already found supporters from the scientific community.

1.1.3 RECENT BIOFUEL PRODUCTION

The EU produced an estimated 768 million gallons of biofuel in 2004 compared with the US (United States) biofuel production of 3.4 billion gallons (mostly ethanol). Biodiesel accounted for nearly 80% of the EU biofuel production. Germany produced over half of the EU biodiesel. France and Italy are also important biodiesel producers, while Spain is the EU leading bioethanol producer (Schnepf, 2006).

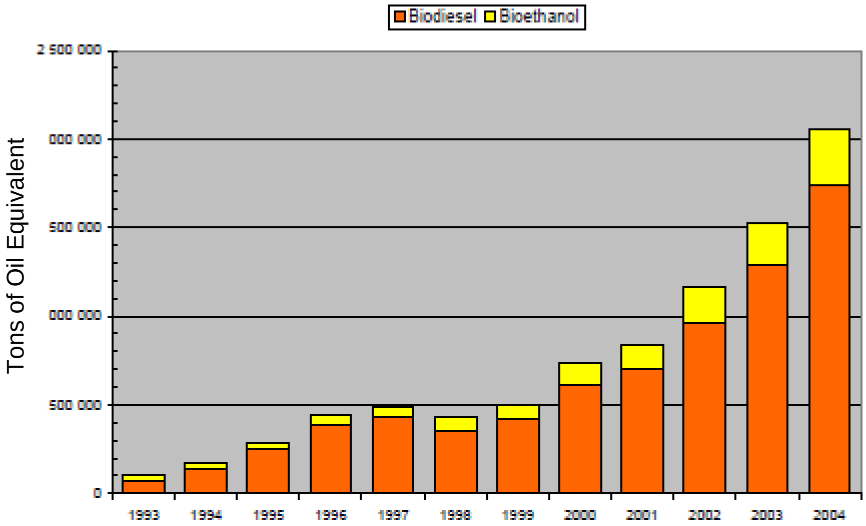


Figure 1-1. Biofuel production in EU since 1993 (2004: EU-25) (Biofuels Research Advisory Council)

The supply of feedstocks is crucial to the success of the EU biofuel strategy, because they represent the primary cost component in the biofuel production process. The major feedstock for the EU biodiesel production has been the rapeseed oil, although almost any vegetable oil or animal fat (including restaurant deep-fry grease) is viable. In 2004, the EU biodiesel production used about 4.1 million metric tons (MMT) of rapeseed. In 2004, the EU harvested oilseeds area was estimated 7.5 million hectares (MHA), out of which 60% was rapeseed, 29% sunflowerseed and 4% soybeans (Schnepf, 2006).

The EU bioethanol is generally produced using a combination of sugar beets and wheat. In 2004, the EU bioethanol production used 1.2 MMT of cereals out of the total EU production of over 289 MMT of grains and 1 MMT of sugar beets out of 123.5 MMT of the sugar beet production. In the long run, abundant domestic supplies and production potential for cereals and sugar beets suggest that bioethanol production likely has greater potential in the EU than biodiesel does. However, high-production costs of the EU-produced biofuels (primarily due to high-priced internal feedstocks) in comparison with the fossil fuels remain a major impediment to the market-based expansion of the EU biofuel production, particularly for bioethanol. According to the European Commission (EC), the EU-produced biodiesel breaks even at oil prices of around 60€ ($71.60) per barrel, while bioethanol becomes competitive with oil prices of about 90€ ($107.37) per barrel. During February 2006, a barrel of oil — Europe Brent spot price FOB — was quoted at $60.73 per barrel (Schnepf, 2006).

Looking beyond 2010, biofuels could play a more significant role if: (a) oil prices further increase, (b) agricultural policies reform, (c) new technological breakthroughs take place and

(d) imports from third countries are challenged (Commission of the European Communities, 2006b).

1.1.4 BIOFUEL PRODUCTION TARGETS

The Biofuels Directive has set as “reference value” targets a 2% market share for biofuels in 2005 and a 5.75% share in 2010. For the EU-25, the target would require 18.6 million tons of oil equivalent (mtoe) of biofuels by 2010 (Commission of the European Communities, 2006b).

The EU-15 Member States are committed to a combined 8% reduction of greenhouse gas emissions by 2008–12 under the Kyoto Protocol and most new Member States have individual targets (Commission of the European Communities, 2006a).

The EU Action Plan on energy, adopted by the EU leaders in March 2007, sets out concrete actions to achieve competitive, sustainable and secure energy system coupled with a major reduction in greenhouse gas emissions by 2020 (Directorate General for the Environment, 2008). They include:

- cutting energy consumption by 20% compared with business as usual levels through a major improvement in the energy efficiency of a wide range of appliances and equipment
- reducing greenhouse gas emissions by at least 20% (compared with the 1990 levels) by 2020
- increasing renewable energy sources share of energy consumption to 20% from around 7% in 2007
- raising biofuels share of petrol and diesel to 10% from around just 1% in 2007
- adopting a policy framework to ensure and promote environmentally safe use of carbon capture and geological storage (CCS) technology. The aim is to deploy the CCS technology in new fossil-fuel power plants, if possibly by 2020.

1.2 BIOFUEL INCENTIVES

The EC is using both legislation and formal directives to promote biofuel production and use within the EU (Schnepf, 2006):

1) **EU Common Agricultural Policy (CAP)**

The EU crop production patterns have been heavily influenced by the CAP, with its high support prices, planting restrictions, intervention buying, stock management and rigid border controls. Presently, the CAP includes rules on agricultural land use as well as a special payment for the production of crops dedicated to biofuels.

2) **Blair House Restrictions**

The 1992 Blair House Memorandum of Understanding (Blair House Agreement) between the United States and the EU helped to resolve a mutual dispute over the EU domestic support programs that impaired the US access to the EU oilseed markets and thus facilitated the completion of the Uruguay Round Agreement for agriculture. Specifically, the Blair House Agreement limits the amount of the EU oilseed production for food on non-set-aside land and for non-food (i.e. industrial or energy) purposes on set-aside land. The set-aside-based oilseed production is restricted to roughly 0.7 MHA. However, the EC believes that, pursuant to CAP reforms undertaken in 2003, it is no longer subject to the Blair House limitations on oilseed production. In 2005, rapeseed production intended for use as biodiesel feedstock was grown on 1.8 MHA including 0.9 MHA of the set-aside.

3) **CAP Land Use Rules**

Under the CAP, EU farmers are required to set aside 10% of their land to qualify for other CAP benefits. Participating farmers receive a set-aside compensation payment. In addition, EU farmers are allowed to plant oilseeds on the set-aside land (subject to Blair House Agreement limitations) as long as it is contracted solely for the production of biodiesel or other industrial products and not sold into either food or feed markets.

4) **Energy Crop Payments**

In 2003, a new round of CAP reforms established a special aid for energy crops grown on non-set-aside land. Energy crops — those grown for the production of biofuels or for use as biomass in the production of electric and thermal energy — were eligible for a premium of 45€ per hectare. To establish a budgetary ceiling on such outlays, the energy payments were to be restricted to a maximum guaranteed area of 1.5 MHA. If fully implemented on 1.5 MHA, the program would cost 67.5 million. In 2005, an estimated 0.5 MHA received the energy crop payment.

5) **Sugar Sector Reform**

On February 20 2006, the EU adopted significant reform measures for its sugar sector, including a 36% cut in the internal sugar support price, elimination of the intervention system of sugar purchases and partial sugar production quota buyback. The sugar reforms could impact biofuel feedstock availability, since they substantially reduce internal sugar beet production incentives. However, much of the potential decline in sugar production could be offset by a drop in EU sugar exports, which are restricted to not more than 1.273 MMT annually (compared with an estimated 7.1 MMT in 2005/06). In addition, two reform provisions are likely to impact positively the availability of sugar beets as a biofuel feedstock. First, sugar beet production now qualifies for both set-aside payments when grown as a non-food crop and for the energy crop aid of 45€ per hectare on non-set-aside area. Second, sugar used for the production of bioethanol will be excluded from sugar production quotas. Despite the reforms, the EU internal sugar prices are expected to remain substantially above international market prices; thus preserving it as an expensive feedstock.

6) **EC Directives**

In the recent years, the EC has attempted to focus increasing attention on the development of the EU biofuels sector. Three principal legislative directives, governing biofuels use, taxation and quality, have been issued recently by the EC to guide Member State agriculture-based renewable energy production.

7) **Biofuels Use Directive**

As already stated before, the EC established a goal of deriving at least 2% of EU transportation fuel from biofuels by the end of 2005, then growing the biofuels share by 0.75% annually until December 31 2010, when it would reach 5.75%. However, the biofuels goal is not mandatory and individual Member States are free to establish higher standards. As a result, the degree of participation varies substantially across the EU Member States. Because the targets are not mandatory, no penalty for non-compliance is involved. However, Member States are expected to report annually those measures undertaken to aid compliance on the sales of both total transportation fuel and the share of biofuels. Despite various State and EU-wide policies designed to support biofuels production, the EU biofuels goal of 2% by 2005 was not achieved. Instead, it appears that biofuels attained a EU-wide share of only about 1.4% of transport fuels.

8) **Energy Taxation Directive**

In 2003, the EU framework for the taxation of energy products and electricity was amended to allow Member States to grant tax reductions and/or exemptions in favor of renewable fuels under certain conditions. These tax concessions are considered as state aids, which may not be implemented without prior authorisation by the Commission. The Commission assessment has the aim of avoiding undue distortions of competition and is based on the Community guidelines on state aid for environmental protection. (Commission of the European Communities, 2006b). To minimize the tax revenue loss for Member States, the final tax on biofuels intended for transport use may not be less than 50% of the normal excise duty.

9) **Fuel Quality Directive**

In 2003, the EU environmental specifications for market fuels were amended to establish specifications for petrol and diesel. The new specifications encompassed the incorporation of biofuels. The European Committee for Standardization (CEN) has set limits on biodiesel blending to no more than a 5% share by volume (or 4.6% in energy terms) for technical reasons. As a result, this appears to be an issue that the EC will need to resolve to achieve its goal of a 5.75% share of transportation fuel by 2010.

Present actions at European level (ERA-NET) in the field of biomass cultivation and utilization aim to further increase the cost-effectiveness of R&D funding through programme coordination and the initiation of joint activities at national and regional level (Commission of the European Communities, 2006b).

The proposal for the Seventh Framework Programme (2007–2013) gives priority to biofuel research to further strengthen the competitiveness of the EU biofuel industry. In the Cooperation Specific Programme research activities will concentrate mainly on two themes (i) “Energy”, aiming at bringing down the unit cost of fuels by improving conventional technologies and developing second-generation biofuels (e.g. Fischer-Tropsch biodiesel, lignocellulosic ethanol, bio-dimethylether) and (ii) “Food, agriculture and biotechnology”, applying life sciences and biotechnology to improving biomass production systems. The concept of biorefineries, aiming at the integral use of the biomass and maximising the cost effectiveness of the final products, will be a key focus in both themes (Commission of the European Communities, 2006b).

1.3 EU VISION FOR BIOFUELS

Looking at the near future (2010), a regulated market-based approach that encourages the development of the EU’s domestic biofuel industry in a balance with imports would bring an average cost of € 6 billion per year in order to meet the indicative target of the Biofuels Directive. Relating this to the gross diesel and gasoline consumption in the EU-25 (334 billion litres in 2002), it corresponds to an average increase of the transportation fuel cost of 1.2 to 2.5 euro cents per litre in order to finance the additional biofuel use targeted for 2010.

The uncertain development of oil prices and the cost of biofuel production make it difficult to quantify the cost to society of reaching the vision for 2030. Preliminary estimates, based on 2005 market prices, suggest that 25% biofuels in road transportation in 2030 could cost an excess of € 31 billion per year, equivalent to an additional 6.6 euro cents per litre of gasoline and 8.2 euro cents per litre of diesel.

In this context, the cost of increased biofuel use to society has to be weighed against the monetary value of the benefits, such as reduced greenhouse gas emissions, diversification of our energy mix, enhanced security of supply and job creation in rural areas. A forwardlooking biofuel strategy with a strong focus on research, development and innovation should be part of a consistent set of research and energy policies which have as their goal a cleaner and sustainable energy future.

Large-scale deployment of biofuels can be expected by 2020-2030. It is nevertheless necessary to identify the intermediate steps and the likely timeline for the development of the new options required for a strong biofuels industry and a significant biofuel use in Europe (Biofuels Research Advisory Council).

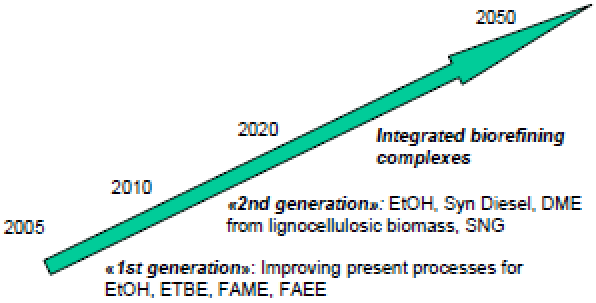


Figure 1-2. Anticipated future roadmap (Biofuels Research Advisory Council)

Liquid biofuels, which are compatible with the current technology, offer the highest potential for the fast introduction of biofuels on a large scale. The preference for liquid fuels from biomass does, however, not mean that there is no place for gaseous fuels in this strategy (Biofuels Research Advisory Council).

2 BIOFUEL PRODUCTION – STATE OF THE ART

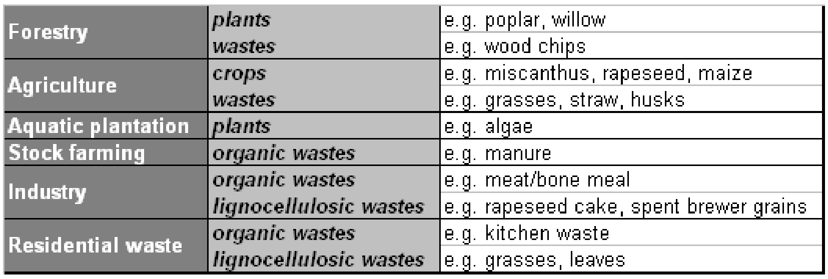
2.1 BIOGENIC RESOURCES

2.1.1 BIOMASS CLASSIFICATION

The biogenic materials classification is a complicated task due to their variety of physical characteristics, chemical characteristics and uses.

The following Table gives a biomass resources overview according to their sector of appearance (e.g. forestry, industry) and their type (e.g. raw material, waste):

Table 2-1: Biogenic materials classification



Forestry	***plants***	e.g. poplar, willow
	wastes	e.g. wood chips
Agriculture	***crops***	e.g. miscanthus, rapeseed, maize
	wastes	e.g. grasses, straw, husks
Aquatic plantation	***plants***	e.g. algae
Stock farming	***organic wastes***	e.g. manure
Industry	***organic wastes***	e.g. meat/bone meal
	lignocellulosic wastes	e.g. rapeseed cake, spent brewer grains
Residential waste	***organic wastes***	e.g. kitchen waste
	lignocellulosic wastes	e.g. grasses, leaves

2.1.2 BIOMASS PHYSICOCHEMICAL COMPOSITION

The physicochemical composition of different biogenic materials may indicate their suitability as feedstocks for different conversion processes. The biogenic materials can be categorized into the following clusters: untreated wood, treated wood, grass/plant, straw (including stalks, cobs, ears), husk/shell/peat, organic residue/product, algae, manure and sludge. A database with information on their ultimate analysis, biochemical composition, ash content, water content, higher and lower heating value is presented in the Annex (IEF Joanneum Research; KF-Uni Graz; Phyllis Biomass Database).

2.1.3 BIOMASS AVAILABILITY

The official data concerning the biomass availability and prices in the EU are limited. Literature references indicated that in 2006, the EU felling residues were estimated to be 173 Mm^3 annually, out of which 63 Mm^3 could be technically available for further use. In addition, 9 Mm^3 stumps could be collected out of 78 Mm^3 in total. Assuming that 25% of the excess growth in commercial forests could be cut for energy use, a total wood-for-energy of 140 Mm^3 annually could be estimated. These figures include the current use, but do not include traditional firewood or industrial/secondary wood (EU Experts Workshop, 2006).

In 2006, the harvested roundwood was more costly, but it typically worth 30 € / m^3 versus 10 € / m^3, which was the price for energy wood (EU Experts Workshop, 2006).

In 2005, the removal of coniferous roundwood species in EU-25 was 317022 Mm^3, while the removal of non-coniferous roundwood species was 108671 Mm^3 (Eurostat, 2007).

In 2003, the actual wheat & barley production in EU was 1000 tonnes/region, the straw production was also 1000 tonnes/region, while the ratio of straw/grain varied from 0.62 to 0.94 (EU Experts Workshop, 2006).

In 2007, the annual selling prices of agricultural products (absolute prices) in EU-27 was in the range of 15.3-23.5 € / 100 kg of soft wheat, 20.3-33.2 € /100 kg of rape and 22.3-42.0 € /100 kg of sugar beet (Eurostat, 2008).

In 2007, the total harvested production in EU-27 was 260302 kt of cereals (including rice), 114810 kt of sugar beet, 18128 kt of rapeseed and 4783 kt of sunflower. The harvested production of the most important cereals was 120253 kt for wheat, 57871 kt for barley, 47532 kt for grain maize, 7992 kt for rye/meslin and 2723 kt for rice (Eurostat, 2008).

2.2 BIOMASS CONVERSION TECHNOLOGIES

Different pathways exist for the conversion of different biomass types. The following graph presents the main biomass conversion processes (thermochemical, biochemical and physichemical), their required level of temperature (high, medium, low) and their products:

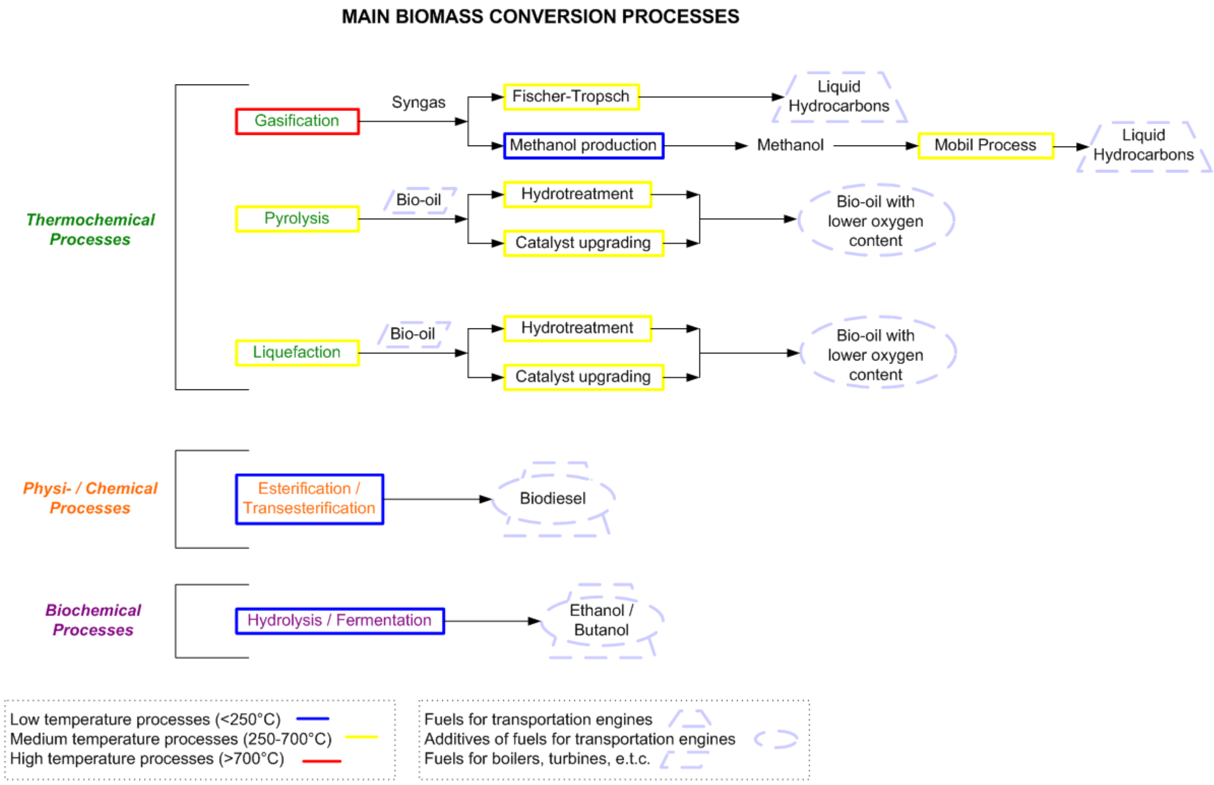


Figure 2-1. The main biomass conversion pathways

The physichemical biomass conversion consists of processes that focus on the utilization of oils/fats for the 1st generation biofuels production (e.g. biodiesel). The biochemical biomass conversion consists of a cluster of processes that use the nature’s media (e.g. enzymes and microorganisms) for the biogenic feedstocks transformation into the 1st and 2nd generation biofuels (e.g. ethanol and butanol). It is not within the scope of the present work to focus on these processes, since they represent a different aspect of the biofuel production in terms of raw materials and auxiliary media. The thermochemical processes can use a wide variety of raw materials for the production of 2nd and 3rd generation biofuels with valuable characteristics.

Gasification, pyrolysis and liquefaction are the three main processes included in the thermochemical biomass conversion. The main characteristics of these processes are summarized in the sections below.

2.2.1 GASIFICATION

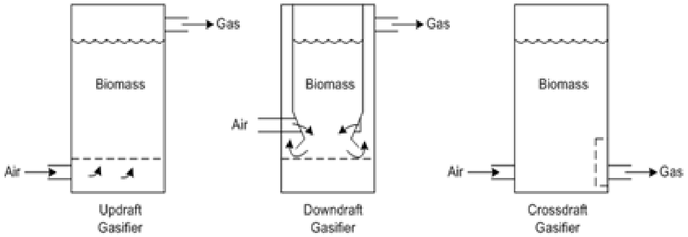
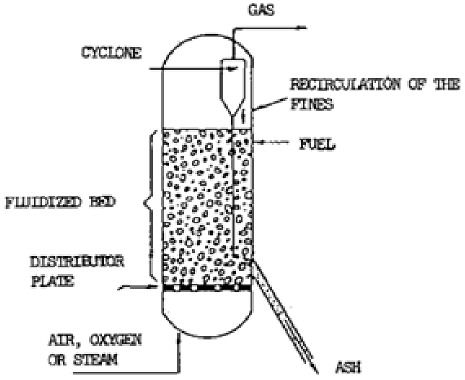
2.2.1.1 DESCRIPTION

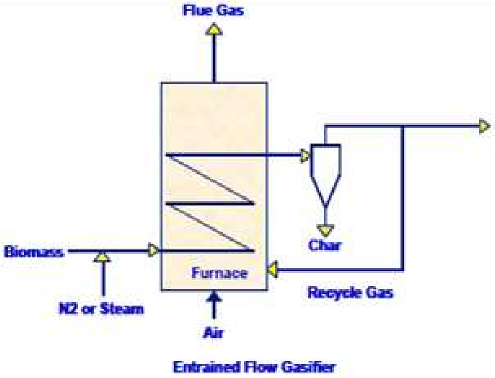
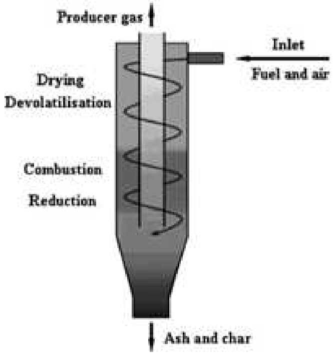
This process requires a high temperature level (>800 ℃): therefore in order to increase its energy efficiency it is not typically designed as a stand-alone process in commercial applications. Research efforts have been employed in order to develop efficient, low cost and reliable gasification systems as well as to design their commercialization, particularly for power generation (Sharma, 2009). Due to the high operating costs, gasification has been facing economic challenges regarding its upscaling to commercial applications (Lappas, 2008). Its main product is syngas (CO_2, H_2), which can be used as a gas fuel. Alternatively, it can be converted into a liquid fuel in a subsequent step, by the Fischer-Tropsch technology (Bridgwater, 1994). The Fischer-Tropsch process advantage is that it produces liquid hydrocarbons, which can be used as a transportation fuel. Still, the gasification high temperature demand and the two-step conversion process requirement for the liquid biofuel production are factors that lower the mass and energy efficiency of this technology.

2.2.1.2 REACTOR TYPES

Gasifiers are classified according to the way the gasification agent is introduced. There are three main gasifier types: the updraft, the downdraft and the crossdraft. The choice of one gasifier type over the other is dictated by the used fuel, its available form, its size, its moisture content as well as its ash content (Yogi Goswami, 1986). Apart from the three main gasifier types, additional ones have been developed. Much experimental work has been done on the fluidized bed biomass gasification using different gasification agents (e.g. air, pure steam, oxygen/steam and air/steam) (Campoy et al., 2009). Entrained flow gasifiers have also been developed. In this case, a pulverised solid fuel is mixed with a steam/oxygen stream and is converted under a turbulent dust flame at high temperatures (>1200 ℃) in a very short time (few seconds) (Henrich and Weirich, 2002). Cyclone gasifiers are a type of entrained flow reactors, used both as gas cleaners and gasifiers. An overview of the gasification reactor types is depicted below:

Table 2-2: Overview of the gasification reactor types (FAO, 1986; Henrich and Weirich, 2002; National Renewable Energy Laboratory; Miccio et al., 2009; Yogi Goswami, 1986; Suna et al., 2009)

Reactor Type	Advantages	Disadvantages	Design
Updraft	▪ small pressure drop	▪ great sensitivity to tar and biomass fuel moisture content	
	▪ good thermal efficiency	▪ poor reaction capability with heavy gas load	
	▪ little tendency towards slag formation		
Downdraft	▪ flexible adaptation of the gas production to load changes	▪ reactor tends to be tall	
	▪ low sensitivity to charcoal dust and biomass fuel tar content	▪ not feasible for very small biomass fuel particle size	
Crossdraft	▪ short reactor height	▪ very high sensitivity to slag formation	
	▪ very fast response time to load changes	▪ high pressure drop	
	▪ flexible gas production	▪ can be operated in very small scale units	
Fluidized bed	▪ fast biomass fuel heating rate	▪ demand for a catalyst with good mechanical properties	 (equipped with an internal cyclone to minimize char blow-out)
	▪ good contact between the biomass and the catalyst	▪ when some biomass fuels are used, problems with feeding, bed instability and fly-ash sintering in the gas channels can occur	
	▪ easy temperature control	▪ poor response to load changes	
		▪ small fluidized bed gasifiers are not foreseen	

Entrained flow	▪ almost tar-free syngas production ▪ leach-resistant molten slag production	▪ high temperature demand ▪ high energy consumption ▪ demand for biomass pre-treatment into powder	
Cyclone air	▪ it can trap the particles and separate the ash (alkali and other heavy metal traces) from the flow	▪ high energy consumption ▪ demand for biomass pre-treatment into powder	

Presently most of the existing biomass gasification technologies can not completely satisfy the industrial application requirements, because of their structural characteristics and the operational conditions (Suna et al., 2009). Therefore, further research is needed.

2.2.1.3 REACTION MECHANISMS

If the complex biomass material must be reduced to a simplified chemical formula, with very small amounts of sulfur and nitrogen that are not considered in terms of overall chemistry, then this formula would be: $CH_{1.4}O_{0.6}$.

Oxygen-blown gasification can be considered to be an incomplete combustion or partial oxidation. Gasification using a minimum amount of oxygen can be described by the following reaction:

$$CH_{1.4}O_{0.6} + 0.2\ O_2 \rightarrow CO + 0.7\ H_2$$

In cases where no oxygen is used, the gasification reaction can be described by the following reaction:

$$CH_{1.4}O_{0.6} \rightarrow 0.6\ CO + 0.4\ C + 0.7\ H_2$$

This reaction is endothermic and heat is needed for its initialization. The heat is provided by the oxidation reactions shown above or by indirect heat transfer. Although these ideal reactions are simple, the actual gasification is more complex. Intermediate compounds, such as benzene, tars, methane and other light hydrocarbons are formed, that must be further processed if the syngas is to be used in high efficiency power applications or biofuel production processes (National Renewable Energy Laboratory).

The water gas shift reaction is a reaction that results in the formation of unwanted CO_2, but it can be used to shift the H_2:CO ratio of the incoming syngas:

$$H_2O + CO \rightarrow H_2 + CO_2$$

The Fischer–Tropsch process involves a variety of competing chemical reactions, which lead to a series of desirable products and by-products. The most important reactions are those resulting in the formation of alkanes. These can be described by chemical equations of the following form:

$$(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+2)} + n\ H_2O$$

The simplest of these (n=1) results in the formation of methane, which is generally considered an undesirable by-product (particularly when methane is the primary feedstock used for the syngas production). Process conditions and catalyst composition are usually chosen to favor higher order reactions (n>1) and thus minimize methane formation. Most of the alkanes produced tend to be straight-chained, although some branched alkanes are also formed. In addition to the alkane formation, competing reactions result in the formation of alkenes as well as alcohols and other oxygenated hydrocarbons.

2.2.1.4 MASS AND ENERGY EFFICIENCY

The gasification energy efficiency can vary according to the used feedstock and the process characteristics. Assuming optimum conditions, the energy efficiency from wood (with 35% moisture) to 40 bar syngas (with H_2/CO equal to 2) is 81%, calculated based on the Lower Heating Values (LHVs). If the net electricity production is included (calculated to the primary energy with 40% efficiency), the overall efficiency is 84%. Alternatively, two options can be selected to pre-treat biomass before gasification: (a) torrefaction to produce torrefied wood or (b) fast pyrolysis to produce oil/charvslurry respectively. These combined systems show lower energy efficiency (overall efficiency is approximately 75%), higher investment costs and more complexity, but pressurizing and feeding systems become conventional compared with those of sole gasification (Van der Drift et al., 2004). Efforts should be focused on minimizing the clean syngas production cost (Spath and Dayton, 2003).

Fischer-Tropsch plants exist in South Africa, Malaysia, New Zealand (Spath and Dayton, 2003) and Germany (Choren, 2008). Shell has been financing the research work of the company Choren on the Gasification / Fischer-Tropsch combined process. Choren has been building the world’s first commercial plant in Freiberg, Saxony. The biomass to liquid fuel (SunDiesel) efficiency of this developed process is reported to be ~20% (Choren, 2008).

2.2.2 PYROLYSIS

2.2.2.1 DESCRIPTION

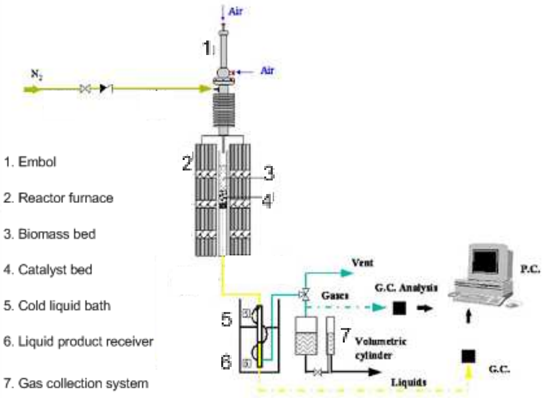
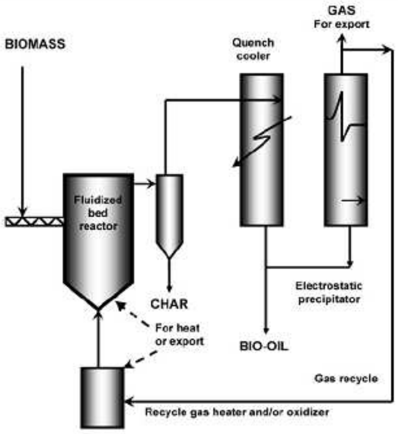
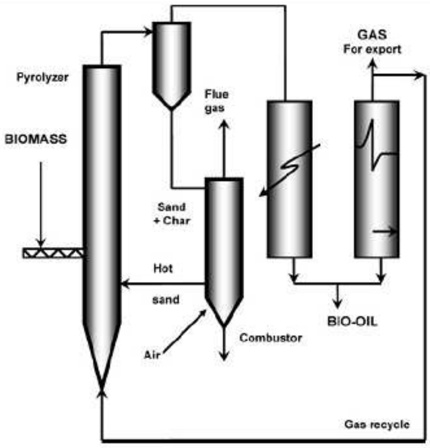
There are different versions of this process, depending on the used operational parameters: (1) slow pyrolysis, (2) conventional pyrolysis, (3) flash pyrolysis and (4) fast pyrolysis. Specific interest is focused on the flash pyrolysis, which can maximize the liquid product yield (70% wt.). Another pyrolysis version is the vacuum flash pyrolysis: in this case, conversion is performed under vacuum to limit the secondary decomposition reactions; therefore, a high oil yield and a low gas yield is accomplished (Zeevalkink, 2005). The pyrolysis liquids are non-thermodynamically controlled products and optimal residence times and temperatures are necessary to freeze the desired intermediates. The pyrolysis liquid (bio-oil) has a high oxygen content, which makes it less attractive as a liquid fuel. This high oxygen content is responsible for its unusual characteristics, such as water miscibility and temperature sensitivity. Bio-oil can be used in motors and turbines, while its use as a transportation fuel requires further upgrading to improve its fuel properties (Huber and Corma, 2007). Currently, there are two different upgrading methodologies: (a) the modified conventional bio-oil hydrotreating to a naphtha-like product that can be characterized as CH_2, or (b) the bio-oil zeolite cracking and the highly aromatic product synthesis, which can be characterized as $CH_{1.2}$ (Bridgwater, 1994).

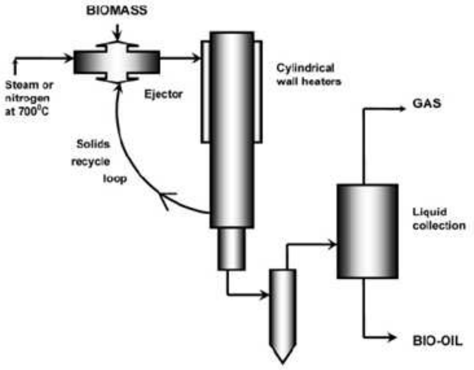
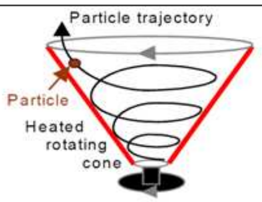
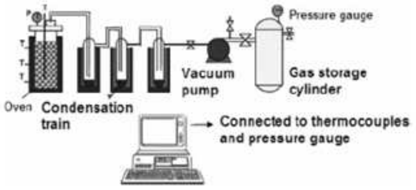
2.2.2.2 REACTOR TYPES

At the heart of the fast pyrolysis process is the reactor. Although it probably represents at most only about 10-15% of the total capital cost of an integrated system, most research and development projects have focused on the reactor. Increased attention is now being paid to the liquid quality control and improvement as well as the collection systems improvement. The rest of the process consists of the biomass reception, storage and handling, the biomass drying and grinding, the product collection and storage as well as, when relevant, the liquid upgrading (Bridgwater, 2006).

Different types of pyrolysis reactors exist apart from the simple fixed bed reactor. Bubbling fluid bed reactors are fluidized bed reactors. Their difference with the circulating fluid bed reactors is that the char residence time of the latter is almost the same as for vapours and gases and the char is more attrited, due to higher carrier gas velocities. The ablative pyrolysis is substantially different in concept from the other fast pyrolysis methods. In all the other methods, the reaction rate is limited by the heat transfer rate through the biomass particles, which is why small particles are required. In ablative pyrolysis, heat is transferred from the hot reactor wall to “melt” wood, that is in contact with it under pressure. The reaction rate is strongly influenced by the pressure, the biomass relative viscosity and the heat exchange surface as well as the reactor surface temperature. Entrained flow fast pyrolysis is in principle a simple technology, but most developments have not been as successful as had been hoped, mostly because of the poor heat transfer between the hot gas and the solid particle (Bridgwater, 2006). Screw reactors have been recently developed for the pyrolysis process. The screw can be single or twin. A fast twin screw flash pyrolysis reactor has been developed. The objective was to produce a high yield of a transportable bio-oil/char slurry for subsequent large scale gasification (Bridgwater, 2004). BTG has developed a rotating cone biomass pyrolysis reactor. This reactor operates with centrifugation principles and uses sand as an auxiliary medium. Centrifugation drives hot sand and biomass up the rotating heated cone. Vapours are condensed, the char is burned and hot sand is re-circulated (Czernik, 2004). A pyrolysis reactors overview is depicted below:

Table 2-3: Overview of the pyrolysis reactor types (Adam et al., 2006; Antonakou et al., 2006a; Bridgwater 2004; Bridgwater, 2006; BTG World, 2009; Czernik, 2004; Demiral and Şensöz, 2008; Gayubo et al., 2005; Mohan et al., 2006; Pütün et al., 2006; Vitolo et al., 1999)

Reactor Type	Advantages	Disadvantages	Design
Fixed bed	▪ simple design	▪ concentration and temperature gradients	
	▪ simple construction and operation	▪ no mixing is possible	
Bubbling fluid bed	▪ well-understood technology	▪ demand for small biomass particles (<2-3 mm)	
	▪ simple in construction and operation		
	▪ good temperature control	▪ the biomass particle heating rate is usually the rate-limiting step	
	▪ very efficient heat transfer to biomass particles		
Circulating fluid bed	▪ the same advantages like in bubbling fluid bed reactors	▪ heat transfer in large throughputs may be challenging	
	▪ is potentially suitable for very large throughputs		

Ablative	▪ large biomass particels can be used (no upper size limit)	▪ the process is surface area-controlled	
	▪ no demand for an inert carrier gas	▪ upscaling is a linear function of the heat transfer area	
	▪ processing equipement is smaller and of potentially lower cost	▪ the reactor is mechanically driven and therefore more complex	
Entrained flow	▪ simple technology	▪ demand for high relative gas velocities and high turbulence ▪ requires large plant sizes	n.a.
Screw	▪ possibility to create zones of different temperatures ▪ efficient biomass particles mixing ▪ possibility to regulate the biomass particles residence time inside the reactor ▪ simultaneous reactor cleaning	▪ long reactors	n.a.
Rotating cone reactor	▪ intense mixing	▪ the heat transfer to the bed has yet to be proven at large scale	
	▪ no demand for an inert carrier gas	▪ demand for small particle sizes	
Vacuum reactor	▪ volatile molecules residence time is not coupled to the biomass particles residence time ▪ a short volatiles residence time is easily achieved	▪ poor heat and mass transfer rates	
	▪ no demand for a carrier gas	▪ demand for larger-scale equipment	

None of the reactor concepts described above, in their present state of development, fully satisfy the requirements for a promising biofuel production methodology with a reasonably trouble-free operation, scaling up potential and economically competitive performance (Mohan et al., 2006). Further research will be necessary to optimize reactor types according to the different application requirements.

2.2.2.3 REACTION MECHANISMS

Pure cellulose pyrolysis produces mainly levoglucosan, probably by a mechanism involving intramolecular condensation and sequential depolymerization of the glycosidic units, as shown in the following Figure (Huber et al., 2006):

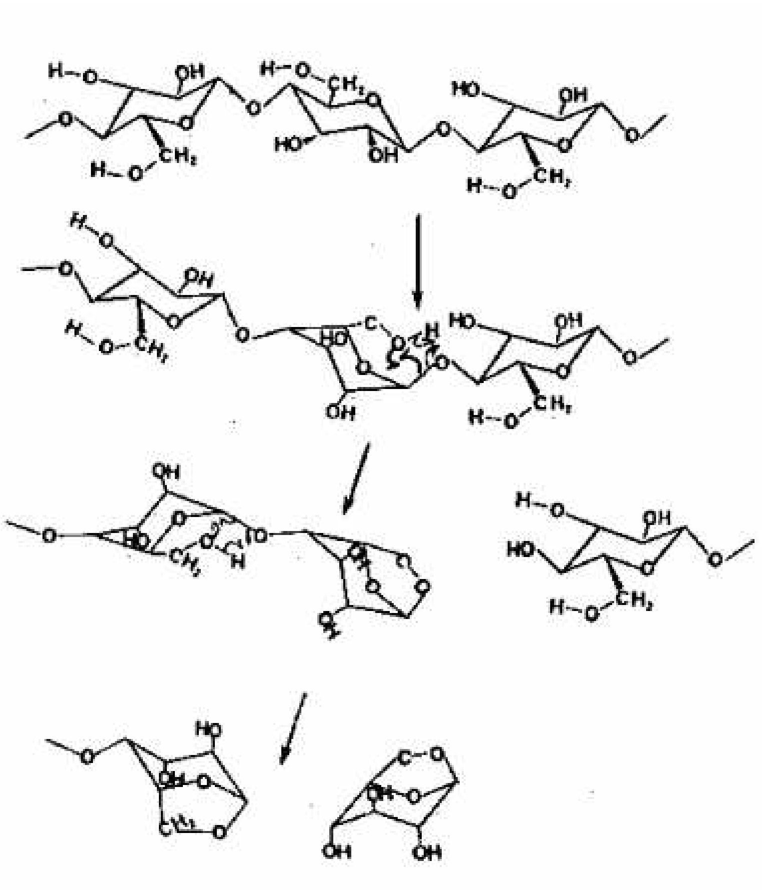


Figure 2-2. Mechanism of cellulose degradation without alkali metals (Huber et al., 2006)

The biomass pyrolysis, at the medium temperature range of 250-700 °C, can produce a liquid product with the following empirical formula (Bridgwater, 1994):

$$C_6H_{12}O_6 \rightarrow C_6H_8O_4 + 2\ H_2O$$

Inorganic impurities present in the biomass play a key role in terms of the bio-oil product selectivity. The addition of minor amounts of alkali (such as K, Li, Ca) to cellulose shifts the mechanism (and the final product selectivity) so that glycolaldehyde is the stable reaction intermediate instead of levoglucosan (Huber et al., 2006).

The exact mechanism where trace quantities of salts and metal ions influence the pyrolysis course is not known, although a probable mechanism is shown in the following Figure.

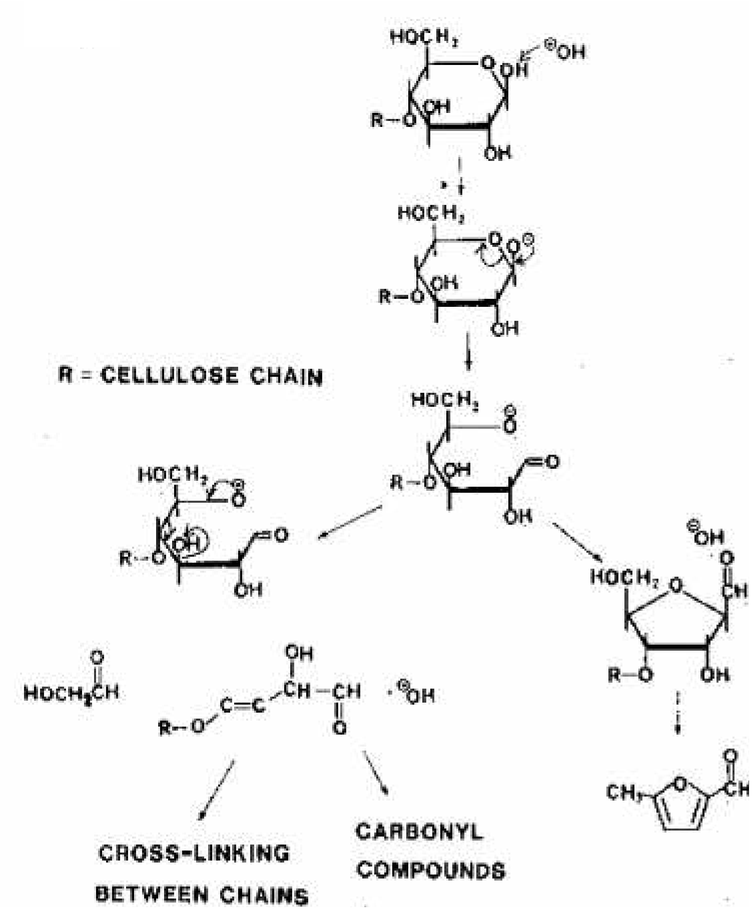


Figure 2-3. Glucose degradation with alkali metal catalyzed or glycoside rupture pathways (Huber et al., 2006)

The pyrolysis behavior of sugars is different than that of cellulose even though they have similar chemical structures (Huber et al., 2006).

A possible mechanism for the thermal decomposition of soybean oil is shown in the following Figure. The exact thermal decomposition mechanism is very complex, generating a wide range of structures (Huber et al., 2006):

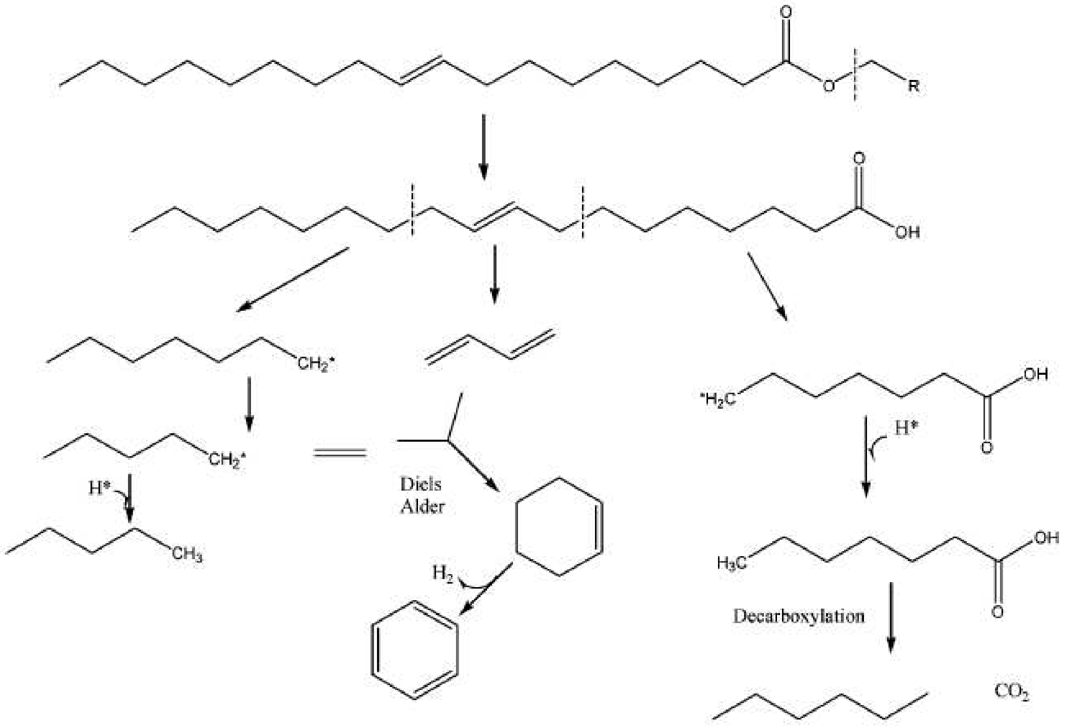


Figure 2-4. Mechanism of triglycerides pyrolysis (Huber et al., 2006)

2.2.2.4 MASS AND ENERGY EFFICIENCY

The pyrolysis conversion mass balance is significantly affected by the operational parameters used during the conversion. Slow pyrolysis favours the charcoal production at the expense of gas and liquid. The maximum charcoal yield is ~30%. Conventional pyrolysis produces approximately equal quantities of liquid, gas and charcoal. Flash pyrolysis maximizes liquid yields (up to 70% wt.), while the fast pyrolysis maximizes gas yields (up to 80% wt.). The energy efficiency data collection of pyrolysis systems is challenging due to the variety of raw materials and available technologies that result in different numbers. The pyrolysis has a lower capital cost than liquefaction and many pyrolysis technologies are currently being used commercially (Huber and Corma, 2007).

2.2.3 LIQUEFACTION

2.2.3.1 DESCRIPTION

This cluster contains a wide variety of processes. We could classify them in two general categories: (1) the hydrothermal processes, when water is used as a liquid carrier for the biomass conversion and (2) the solvolysis processes, when organic liquids are used as liquid carriers (Bridgwater, 1994). High pressure is often applied in liquefaction processes to avoid the evapouration of the liquid carrier. Therefore, the liquefaction processes commercialization is quite challenging due to high investment costs (Bridgwater, 1994). Often, liquefaction appears to produce a liquid product with a lower oxygen content (16% wt.) than that of pyrolysis liquid (35-40% wt.) (Bridgwater, 1994).

Some characteristic liquefaction technologies are displayed below. All information concerning the product quality and yields are based on the process developers statements:

- *HydroThermal Upgrading (HTU):*

The HTU process is a hydrothermal liquefaction process that runs at 300-350 ℃, at 120-200 bar, with 5-20 min residence time. Different types of dry or wet biomass can be used to produce 45% wt. of biocrude. The thermal efficiency of the process ($\eta_{th} = LHV_{biocrude\ output} / (LHV_{of\ feed} + LHV_{of\ used\ external\ fuel})$) is reported to be ~75% (Naber and Goudriaan).

- *Aqueous Phase Dehydration/Hydrogenation (APD/H):*

This catalytic process can be used to convert biomass-derived oxygenated hydrocarbons into alkanes, at low temperatures (150-265 ℃). Alkanes, ranging from C1 to C6, can be produced by aqueous-phase dehydration/ hydrogenation (APD/H). Liquid alkanes, ranging from C7 to C15, can be produced by combining the dehydration/hydrogenation process with an upstream aldol condensation step to form C–C bonds. The dehydration/hydrogenation step takes place over a bi-functional catalyst (4 wt.% $Pt/SiO_2–Al_2O_3$) containing acid and metal sites in a specially designed four-phase reactor. An aqueous inlet stream containing the large water-soluble organic reactant, a hexadecane alkane sweep stream and a H_2 inlet gas stream is employed. The hexadecane sweep stream is used to remove the products from the catalyst as valuable components before they go on further to form coke (Huber et al., 2006).

- *NTK-Process (FH Gießen)*

This process runs at atmospheric pressure, at a temperature level of 350-400 ℃, in the presence of catalysts and in the absence of oxygen. The process was developed to convert sewage sludge and meat and bone meal. The products are claimed to be aliphatic hydrocarbons (C5-C20), carbon residue with minerals, non condensable gases (C1-C4, CO_2)

and reaction water with dissolved salts. The condensate is separated via centrifuge into reaction water, organic liquid and powder (Let, 2007).

- *B/M-Process (Mueborit)*

The main objective of this process was not to produce liquid fuels according to transportation fuel standards, but to convert biomass into a liquid fuel that could be an alternative to heating oil or that could be used as raw material for further synthesis. Lignin is converted into soluble phenol derivatives, the molecular size of cellulose is reduced and the lignocellulosic bonds are dissolved by using solvolysis. Lignocelluloses are decomposed in a discontinuous agitating tub with 5 bar overpressure and a temperature below 200 °C in a potassium carbonate hydrate molten bath. Organic compounds (density: ~1.5 kg/m^3) can be separated from the slurry phase by a column. The final product is a dark brown mixture of various compounds. The highest energetic yield is in the range of 35-37 MJ/kg. The residual slurry contains organic and polar substances and is used as a fuel to supply energy for the process.

- *BFH-Process (BFH)*

This process deals with the conversion of lignocellulosic feedstocks into liquid products by a thermal pressurized treatment. Different reaction systems, retention times, temperature and pressure ranges as well as solvents, catalysts and reducing gases were tested. In the most promising version, the catalytic hydrogenolysis with the use of hydrogen, noble metal catalyst and carrier oil was used. Within a semi-continuous reaction system of three connected autoclaves, it is possible to convert wood (100% wt.) and hydrogen (4% wt.) into 36% wt. oil, 25% wt. aqueous phase, 5% wt. charcoal and 38% wt. gaseous products. The C1-C4 fraction of the occurring gas phase (approx. 17% wt.) is partially treated via the water gas shift reaction to gain the required hydrogen.

- *KDV-Process (Dr. Koch, Prof. Willner)*

The KDV process (Katalytische Druklose Verölung) is a low pressure, medium temperature catalytic process that claims to convert biogenic, crude oil-based and other carbonaceous feedstocks as well as residues into liquid fuels in the range of diesel and gasoline. The process runs at a temperature level of 290-370 °C and at atmospheric pressure or slight vacuum. The used catalysts are Y-type zeolites (Alphakat, 2007).

The pre-treated feedstock is mixed with the liquid carrier and the catalyst in powder form. The vapour products leave the reactor continuously and enter a hydrocyclone, where they are separated from the solid particles. After leaving the cyclone, the gas phase passes a water-cooled condenser, where the water is separated. Finally, the condensate is led into a distillation column, where the remaining water is separated from the oil and different oil fractions are collected. The remaining mixture of the liquid carrier and the solid particles is heated and pressed, whereby a large part of liquid carrier can be recycled into the process. The occurring vapours are also fed into the distillation column. The remaining paste is dried and pressed into pellets, that have a higher energy content than wood chips pellets. The partially recycled liquid carrier is mixed with new feedstock and enters the reactor again. Within the existing Alphakat pilot plant set-up (capacity: 500 l/h), a combined heat and power unit with 230 kW is included. It uses 10% of the produced fuel to provide the process with electricity and thermal energy. Additionally, the non-condensable gases are mixed with the combustion air (Behrendt, 2006). The liquid carrier provides a good heat transfer and a homogenous feedstock heating. A petroleum-based oil (e.g. vacuum gasoil) was used as a liquid carrier.

Unfortunately, there are no reliable data regarding the mass and energy balances or the detailed product chemical composition. According to the developers, the biogenic feedstocks usage leads to an energy efficiency of ~30% (on dry biomass weight) (Behrendt, 2006).

- *DoS-Process (Prof. Willner)*

The DoS process (Direct liquefaction of organic Substances) is a thermochemical process that converts organic substances into liquid fuels. The conversion takes place under pressure (80 bar), in the presence of a hydrogen atmosphere and at a moderate temperature range of 350-500 °C. The setup and system layout is similar to the KDV process described above, but hydrogen is added into the system. In comparison to the KDV process, the catalysts use is non-compulsory in the DoS process. The used feedstock within this application is a lignin-rich biomass type, like wood, miscanthus or straw.

The dried and milled biomass is fed into the reactor by a screw conveyor. Within this kind of extruder, the feedstock is pre-heated and mixed with recycled heavy bio-oil from the reactor. Before the liquid products are distilled into diesel, gasoline and aqueous fractions, they are separated from the solid particles and the other gaseous by-products. The heavy oil and charcoal particles are recycled into the extruder. The other product gases can be used to provide energy for the process. The solid residue is used together with the aqueous phase to produce hydrogen, which is consumed within the process. This is accomplished via steam gasification with a combined CO-conversion. In this way, it is possible to run the process autarkic in terms of energy and hydrogen demand. The oil yield is ~33% (on dry biomass weight), which leads to an energy efficiency of ~70%, considering an oil mixture LHV of 40 MJ/kg. In a laboratory scale, the produced charcoal is in a range of 10% wt. of the dry biomass. It has been stated by the developer that the formation of charcoal can be almost completely avoided within in a larger scale plant (Willner, 2005; Willner, 2007).

2.2.3.2 REACTOR TYPES

Due to the large variety of liquefaction systems and operational parameters, it is challenging to make an overview of the used reactor configurations.

2.2.3.3 ORGANIC LIQUID CARRIER EFFECT

The organic liquid carrier used in liquefaction technologies can play a chemical role during the biomass conversion, apart from its role as a heat transfer medium.

Biomass can be viewed as a hydrogen-deficient molecule when compared with petroleum-based feedstocks. The maximum theoretical yield of the desired olefin or aromatics is a function of the effective hydrogen-to-carbon ratio (H/C_{eff}) of the feed. The H/C_{eff} ratio is defined as:

$$H/C_{eff} = (H-2O-3N-2S) / C$$

where H, C, O, N and S correspond to the moles of hydrogen, carbon, oxygen, nitrogen and sulfur, respectively, that are present in the feed.

A decrease in the H/C_{eff} ratio of the feed results in a decrease in this yield (Huber and Corma, 2007).

Decarbonylation and decarboxylation reactions are reactions that produce compounds with a higher H/C_{eff} ratio. Aldehydes undergo decarbonylation reactions to produce CO and a decarbonylated product that has an increased H/C_{eff} ratio. Acids can undergo decarboxylation reactions to produce CO_2 and a decarboxylated product that has an increased H/C_{eff} ratio (Huber and Corma, 2007).

Hydrogenation, hydrogen transfer and decarbonylation are the key reactions that can enrich the products H/C_{eff} ratio. Hydrogen transfer reactions occur in the fluid catalytic cracking (FCC) of petroleum-derived feedstocks. The typical reaction involves a hydrogen donor (e.g. a naphthene) and a hydrogen acceptor (e.g. an olefin). When only biomass-derived products are fed into a FCC unit, another hydrogen source is required, if products with enriched H/C_{eff} ratio are desired (Huber and Corma, 2007).

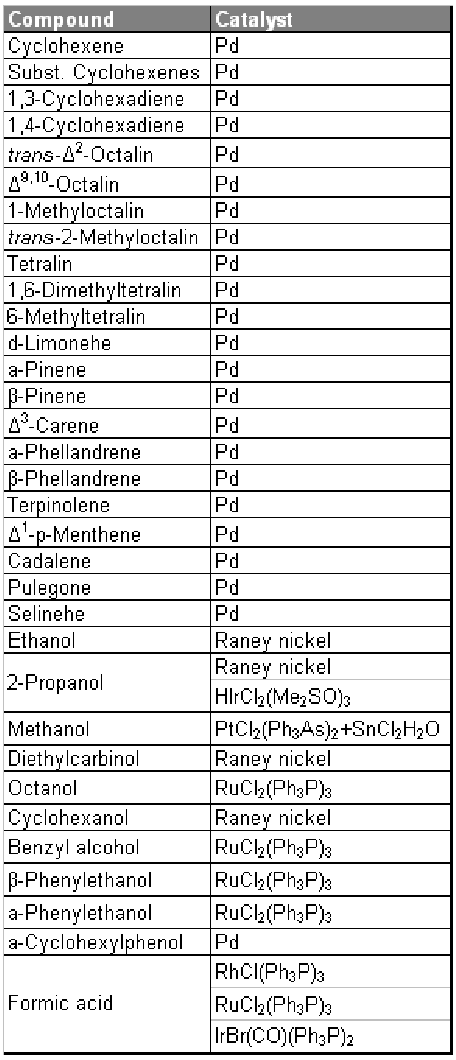
It has been reported that hydrogen could be transferred from petroleum feedstocks to biomass feedstocks during the catalytic cracking of such mixtures (Huber and Corma, 2007).

Hydrogenation reactions usually occur on metal surfaces, where H_2 is dissociated and then undergoes reaction. Metal or metal impurities on a zeolite surface may dissociate H_2, which could then be used for hygrogenation reactions. Alkenes, aromatics, aldehydes and ketones can be hydrogenated with acid catalysts (Huber and Corma, 2007).

It is also possible to achieve the multiple bonds reduction with the aid of an organic molecule as the hydrogen donor in the presence of a catalyst. This process is known as catalytic transfer hydrogenation. The choice of donor is generally determined by its ease of reaction and availability. The chosen compounds can be hydroaromatics, unsaturated terpenes and alcohols (Brieger and Nestrick, 1974).

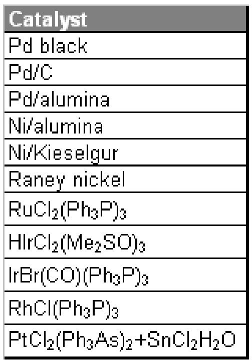
The following Table lists most of the reported hydrogen donors and the used catalysts:

Table 2-4: (a) Hydrogen donor compounds and (b) catalysts used for transfer hydrogenation (Brieger and Nestrick, 1974)



(a)

Compound	Catalyst
Cyclohexene	Pd
Subst. Cyclohexenes	Pd
1,3-Cyclohexadiene	Pd
1,4-Cyclohexadiene	Pd
trans-Δ^2-Octalin	Pd
$\Delta^{9,10}$-Octalin	Pd
1-Methyloctalin	Pd
trans-2-Methyloctalin	Pd
Tetralin	Pd
1,6-Dimethyltetralin	Pd
6-Methyltetralin	Pd
d-Limonehe	Pd
a-Pinene	Pd
β-Pinene	Pd
Δ^3-Carene	Pd
a-Phellandrene	Pd
β-Phellandrene	Pd
Terpinolene	Pd
Δ^1-p-Menthene	Pd
Cadalene	Pd
Pulegone	Pd
Selinehe	Pd
Ethanol	Raney nickel
2-Propanol	Raney nickel
	$HIrCl_2(Me_2SO)_3$
Methanol	$PtCl_2(Ph_3As)_2$+$SnCl_2H_2O$
Diethylcarbinol	Raney nickel
Octanol	$RuCl_2(Ph_3P)_3$
Cyclohexanol	Raney nickel
Benzyl alcohol	$RuCl_2(Ph_3P)_3$
β-Phenylethanol	$RuCl_2(Ph_3P)_3$
a-Phenylethanol	$RuCl_2(Ph_3P)_3$
a-Cyclohexylphenol	Pd
Formic acid	$RhCl(Ph_3P)_3$
	$RuCl_2(Ph_3P)_3$
	$IrBr(CO)(Ph_3P)_2$



(b)

Catalyst
Pd black
Pd/C
Pd/alumina
Ni/alumina
Ni/Kieselgur
Raney nickel
$RuCl_2(Ph_3P)_3$
$HIrCl_2(Me_2SO)_3$
$IrBr(CO)(Ph_3P)_3$
$RhCl(Ph_3P)_3$
$PtCl_2(Ph_3As)_2$+$SnCl_2H_2O$

The solvents effect on the course of the reaction has been studied in a limited number of cases. Temperature appears to be a very critical parameter for the catalytic transfer hydrogenation (Brieger and Nestrick, 1974).

A number of different catalysts have been used during the catalytic transfer hydrogenation reactions. Comparing the effectiveness of various catalysts, clearly palladium is the most effective. Under the standardized conditions where palladium is effective, neither platinum nor rhodium catalysts work (at least at temperatures below 200 ℃). The exceptional palladium role in hydrogen transfer reactions appears to be due to its general mobilizing action for hydrogen-carbon bonds. Commercially available catalysts are perfectly adequate for transfer hydrogenation. Catalysts used for homogeneous hydrogenation have also been used for transfer hydrogenation. Hydrogenolysis frequently accompanies the reduction of multiple bonds (Brieger and Nestrick, 1974).

The dehydrogenated donors, such as benzene or naphthalene, cause no more problems than their usual removal with an inert solvent (Brieger and Nestrick, 1974). In the case of the biofuel production, the hydrogen donor should be of biogenic origin. Additionally, the dehydrogenated donor should have a chemical composition with a high added value as a biofuel component, if its removal is undesirable due to economic reasons.

2.2.3.4 REACTION MECHANISMS

Due to the fact that few publications have focused on the reaction mechanisms of biomass liquefaction, it was possible to retrieve little information on this. The decomposition pathways of cellulose and glucose in supercritical water is shown in the following Figure:

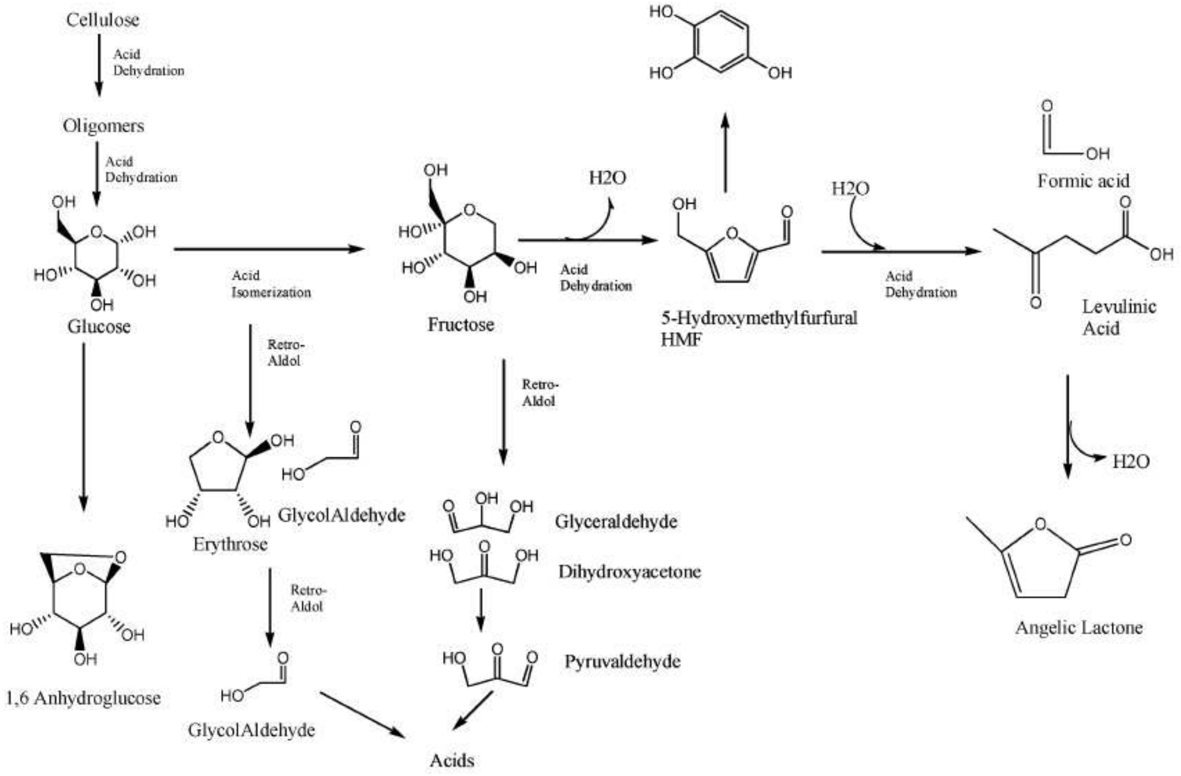


Figure 2-5. Cellulose decomposition pathways in supercritical water (Huber et al., 2006)

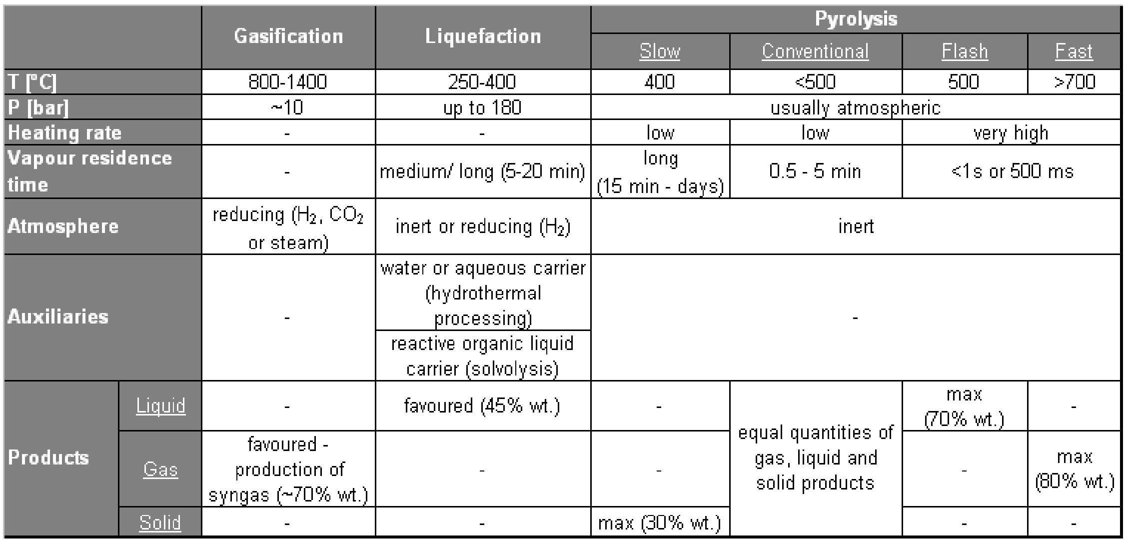
Hemicellulose undergoes analogous reaction pathways to those shown below (Huber et al., 2006).

2.2.3.5 MASS AND ENERGY EFFICIENCY

Any available data on the mass and energy efficiency of different liquefaction technologies are already displayed during the technologies description(see section 2.2.3.1).

An overview of the thermochemical conversion technologies and their characteristic parameters is depicted in the following Table:

Table 2-5: Overview of the thermochemical conversion technologies (Bridgwater, 1994; Demirbaş, 2001; Goyal, 2008, Zeevalkink, 2005)



		Gasification	Liquefaction	Pyrolysis			
				Slow	Conventional	Flash	Fast
T [°C]		800-1400	250-400	400	<500	500	>700
P [bar]		~10	up to 180	usually atmospheric			
Heating rate		-	-	low	low	very high	
Vapour residence time		-	medium/ long (5-20 min)	long (15 min - days)	0.5 - 5 min	<1s or 500 ms	
Atmosphere		reducing (H_2, CO_2 or steam)	inert or reducing (H_2)	inert			
Auxiliaries		-	water or aqueous carrier (hydrothermal processing)	-			
			reactive organic liquid carrier (solvolysis)				
Products	Liquid	-	favoured (45% wt.)	-	equal quantities of gas, liquid and solid products	max (70% wt.)	-
	Gas	favoured - production of syngas (~70% wt.)	-	-		-	max (80% wt.)
	Solid	-	-	max (30% wt.)		-	-

The overview of liquid products and their characteristic parameters obtained via thermochemical conversion technologies is depicted in the following Table:

Table 2-6: Overview of the liquid products obtained via thermochemical conversion technologies (Bridgwater, 2003; Czernik, 2004; Czernik and Bridgwater, 2004; De Klerk, 2007; Elliott and Schiefelbein, 1989; Mohan et al., 2006; Schaub, 2005)

		Pyrolysis	Liquefaction	FT Liquid product
Water content [% wt.]		15-30	5.1	major product
Specific gravity		1.2	1.1	0.77
Viscosity [cSt]		40-100 (measured at 40°C and 25% water)	15000 (measured at 61°C)	2
pH		2.3-5.5	-	-
HHV [MJ/kg]		13.9-41	34	-
HLV [MJ/kg]		16.0-19.2	-	44
Chemical composition		water (15-50%), lignin fragments (15-30%), aldehydes (10-20%), carboxylic acids (10-15%), carbohydrates (5-10%), phenols (2-5%), furfurals (2-5%), ketones (1-5%)	-	paraffins: major product, naphthenes: 1%, olefins: 10%, aromatics: 1%, oxygenates: 5-15%, S-species: none, N-species: none, organometallics: carboxylates
Elementary composition [% wt.]	**C**	54-58	73	C_nH_{2n+2} (n: 10-20)
	H	5.5-7.0	8	
	O	35-40	16	
	N	0-0.2	-	
	ash	0-0.2	-	
Use		fuel for producing heat/electricity (e.g. boilers and turbines)	fuel for producing heat/electricity (e.g. boilers and turbines)	transportation fuel

2.2.4 CATALYSIS IN THERMOCHEMICAL CONVERSION PROCESSES

The aim of the catalysts use in biomass conversion is to enhance the produced liquids quality, by lowering the energy barrier for reactions that can produce compounds with high added value, such as fuels and chemicals.

Catalysts can either be added directly into the reactor for the biomass conversion or they can be used to upgrade the liquid products. Research work on the catalysts use already exists and is presently evolving for all thermochemical processes.

Materials that can be used as catalysts are either “natural catalysts”, already integrated into the biomass feedstock in the form of inorganic components (e.g. K, Na), or “added catalysts”, added externally into the reaction system. The catalytic material is solid in most cases, but liquid catalysts could also be used. Solid catalysts can either be natural or artificial.

An overview of the catalytic materials used in the main thermochemical processes is given below:

Table 2-7: Overview of the main thermocatalytic conversion processes (16th Biomass Conference, 2008; Adam et al., 2006; Aho et al., 2008; Antonakou et al., 2006a; Antonakou et al., 2006b; Bridgwater, 1994; Davda et al., 2005; Gayubo et al., 2005; Koch, 2005; Mahfud et al., 2007; Pindoria et al., 1998; Pütün et al., 2006; Spath and Dayton, 2003; Triantafyllidis et al., 2007; Vitolo et al., 1999; Williams and Nugranad, 2000)

Process	Feedstock	Catalyst	Solvent	Product
Gasification	biomass (different types)	dolomite ($CaMg(CO_3)_2$)	-	syngas
		commercial FCC		
		mineral ash		
		Ni-olivine ($Ni(Mg,Fe)_2SiO_4$)		
		glass-ceramic catalyst with transition metals, such as NiO or CoO		
		nickel, precious metals		syngas (without inorganics)
Fischer-Tropsch	syngas	metal-supported catalysts: Fe, Co (Ni, Ru) supported on SiO_2, Al_2O_3, zeolites	-	hydrocarbons
Mobil	methanol	H-ZSM-5 supported on Al_2O_3 binder	-	gasoline
Pyrolysis	beech wood, sawdust, cottonseed cake, miscanthus	equilibrium FCC catalyst (received from a commercial FCC unit)	-	bio-oil with enhanced properties: (a) lower oxygen content, (b) higher thermochemical stability
		clinoptinolite (natural zeolite)		
		Al-MCM-41, Cu-MCM-41, Fe-MCM-41, Zn-MCM-41		
		alkaline ash in wood		
	bio-oil from: rice husks, canadian oak, swedish pine, mixture of canadian oak and swedish pine, spruce wood, miscanthus, synthetic nature (mixtures of acetone/ phenol or methanol/ furfural/ anisole/ cyclopentanone)	H-ZSM-5 zeolite supported on inert Al_2O_3		
		H-ZSM-5		
		H-ZSM-5 and HY zeolites		
		H-ZSM-5 zeolite		
		H-ZSM-5 zeolite supported on clay binder		
		Al-MCM-41, commercial FCC, SBA-15, MSU-S		
Liquefaction (in general)	biomass (wet, dry)	alkaline ash in wood, Na_2CO_3, K_2CO_3, metal catalysts (Ru, Pd, Fe, red mud, massive nickel)	water (hydrothermal processing), organic solvent (solvolysis)	liquid product with lower oxygen content
		HI		
KDV	plastics/bitumen/waste oils	Na, Ca, Mg, K supported on zeolite Y	organic solvent (solvolysis)	diesel oil
	grease/biological oils			
	wood			
	transformer oil, PVC			
APD/H	sugars, polyols	metal-supported catalysts: Ru, Rh, Ni, Pt, Pd, NiSn supported on SiO_2-Al_2O_3, TiO_2, Al_2O_3	water	hydrocarbons, H_2
Hydrotreatment	biomass (different types)	metal-supported catalysts: Co-Mo, Ni-Mo supported on their oxides or Al_2O_3	-	liquid product with lower oxygen content
		sulphided Co-Mo-P supported on Al_2O_3	organic solvent: tetralin (hydrogen donor)	
		homogeneous ruthenium catalysts	use of a biphasic system: water/toluene	
		Co-Mo supported on spinel ($MgAl_2O_4$)	-	

Further focus will be given on the catalysis mechanisms of pyrolysis and liquefaction technologies.

2.2.4.1 CATALYTIC PYROLYSIS AND CATALYTIC LIQUEFACTION REACTION MECHANISMS

Early zeolite cracking research on biomass derived pyrolysis liquid was carried out in conventional mono-functional ZSM-5 catalyst (Bridgwater, 1994):

$$C_6H_8O_4 \rightarrow 4.6\ CH_{1.2} + 1.4\ CO_2 + 1.2\ H_2O$$

One conjectural way of overcoming the hydrogen deficit is through the modification of the catalyst to include a shift component, that can generate in-situ hydrogen from product gases through the water-gas shift reaction. This might be carried out in a bi-functional or multi-functional catalyst that can operate in a carbon limited environment rather than a hydrogen limited one (Bridgwater, 1994):

$$3.6\ CO + 3.6\ H_2O \rightarrow 3.6\ H_2 + 3.6\ CO_2$$

$$C_6H_8O_4 + 3.6\ H_2 \rightarrow 6\ CH_{1.2} + 4\ H_2O$$

Huber and Corma (2007) have suggested that the FCC conversion of oxygenates from biomass-derived feedstocks mainly occurs through the following five reaction classes (as described in the following Figure): 1) dehydration reactions, 2) cracking of large oxygenated molecules to smaller molecules (not shown in the following Figure), 3) hydrogen producing reactions, 4) hydrogen consuming reactions and 5) production of larger molecules by C-C bond-forming reactions (such as aldol condensation or Diels– Alder).

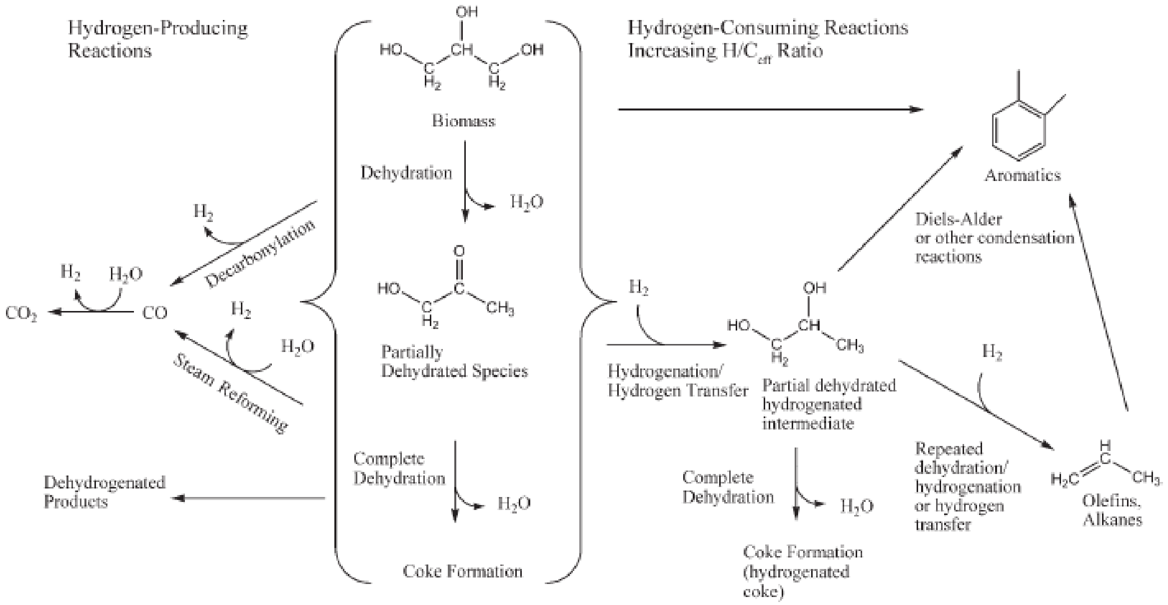


Figure 2-6. Reaction pathways for the catalytic cracking of biomass-derived oxygenates. Note: for dehydrogenation and decarbonylation reactions, the hydrogen can be produced by hydrogen transfer to a hydrogen-deficient molecule (Huber and Corma, 2007)

In this process, H_2 may be produced through steam-reforming, carbohydrates or hydrocarbons dehydrogenation, water gas shift and decarbonylation of the partially dehydrated biomass species. These reactions produce CO, CO_2 and graphitic coke as well as hydrogen. The hydrogen produced in these reactions may be consumed in reactions that increase the products H/Ceff ratio and lead to olefins and alkanes. Hydrogen may be exchanged directly through hydrogen transfer reactions between two hydrocarbon/carbohydrates chains or through consecutive dehydrogenation/hydrogenation processes. Hydrogen-transfer reactions occur on acid sites, while dehydrogenation/hydrogenation reactions are greatly accelerated by the presence of a metal. Aromatics are also produced during this process, possibly by Diels–Alder reactions of partially dehydrated/hydrogenated species. To selectively produce olefins and aromatics, the dehydration, the hydrogen-forming and the hydrogen-transfer reactions must be properly balanced by choosing the proper catalysts and reaction conditions (Huber and Corma, 2007).

The reactivity and reaction pathways for some model bio-oil compounds using ZSM-5 catalysts has been studied:

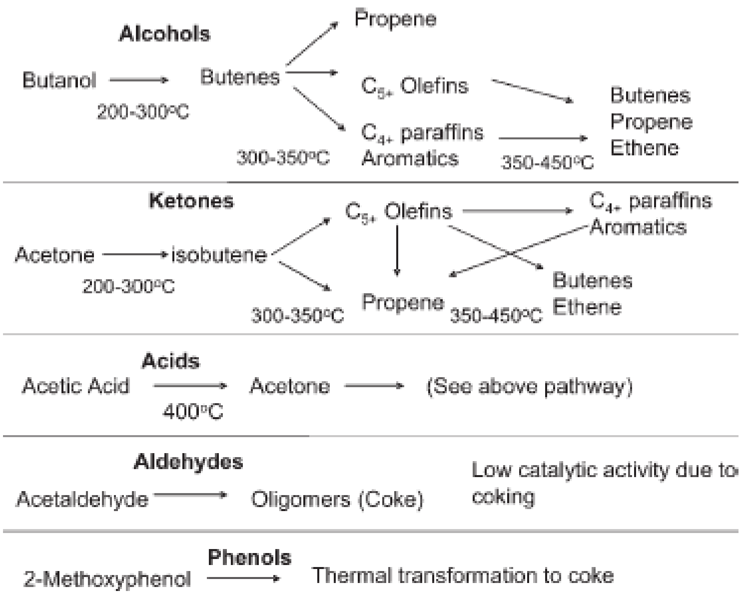


Figure 2-7. The conversion of model bio-oil compounds with ZSM-5 (Huber and Corma, 2007)

These feeds have higher H/Ceff ratios than those of most bio-oils. Nevertheless, these experiments do teach us some of the chemistry involved, since these molecules would be important intermediates of the biomass conversion into olefins and aromatics. Different bio-oils molecules display a significant difference in reactivity and coke formation rates.

Lignin, which consists of polyaromatic oxygenated compounds, is especially challenging to catalytically convert as a result of its stable (non-reactive) aromatic structure. Phenols, which have a chemical structure similar to lignin, produce large molecules of coke on ZSM-5 catalysts (Huber and Corma, 2007).

Vegetable oils catalytic cracking and pyrolysis can be used to produce liquid fuels that contain linear and cyclic paraffins, olefins, aldehydes, ketones and carboxylic acids. Vegetable oils catalytic cracking involves the vegetable oils pyrolysis in the presence of solid catalysts that can improve the product yield. Mainly zeolite catalysts have been tested for this reaction, including H-ZSM-5, Beta zeolite and USY. A reaction pathway for the catalytic cracking of vegetable oils is shown in the following Figure:

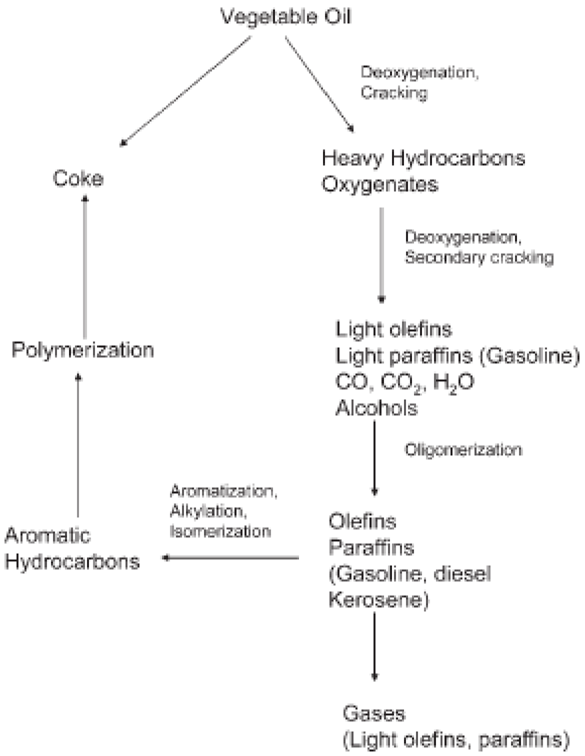
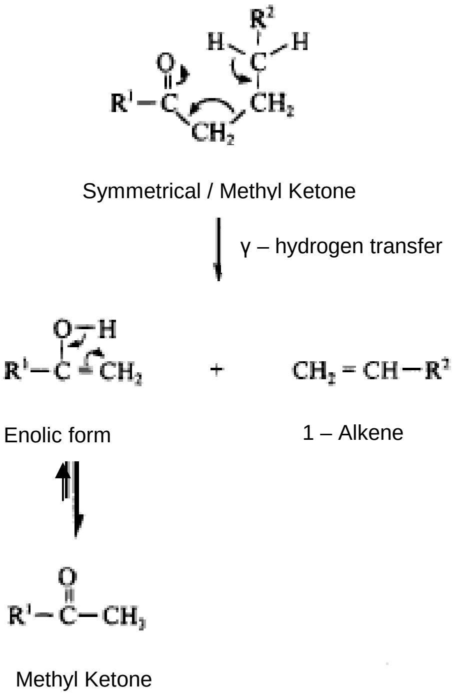


Figure 2-8. Proposed reaction pathway for the cracking of vegetable oils with H-ZSM-5 (Huber and Corma, 2007)

The formation of a symmetrical ketone by the carboxylic acids passing over heated metal oxides at high temperatures is a well-established reaction (Leung et al., 1995):

$$2\ RCO_2H \rightarrow RCOR + H_2O + CO_2$$

It was postulated that the symmetrical ketones generated from the carboxylic acids would undergo a γ-hydrogen transfer mechanism rearrangement to form methyl ketones and terminal alkenes. The enol product is very unstable and it can re-arrange to form the methyl ketone by the process of keto-enol tautomerism. The methyl ketone can also undergo the same mechanism to further produce 1-decene again and acetone. There is an inverse relationship between the hydrocarbon yields and the symmetrical ketone yields (Leung et al., 1995):



i) Diundecyl Ketone, $R^1 = -(CH_2)_{10}CH_3$ $R^2 = -(CH_2)_7CH_3$

ii) 2-Tridecanone, $R^1 = -CH_3$ $R^2 = -(CH_2)_7CH_3$

Figure 2-9. γ-Hydrogen mechanism on the symmetrical ketone and methyl ketone (Leung et al., 1995)

3 THE DEVELOPED PROCESS (KNV)

3.1 MOTIVATION / CONTRIBUTION

Aim of the laboratory tests was to evaluate the effect of catalysts, liquid/solid carriers and operational parameters during the conversion of different types of biomass. The name of the developed process was defined as Catalytic Low Pressure Liquefaction (in german Katalytische Niederdruck Verölung – KNV), with the term liquefaction used in the sense of the one-step (direct) production of liquid biofuel. The role of catalysts during the conversion was studied. The catalytic effect at different points of the conversion process was identified. Different types of biomass were used in the laboratory tests and their suitability as feedstocks for the KNV process was evaluated.

3.2 THE EXPERIMENTAL KNV UNIT AND PROCEDURE

3.3.1 Experimental unit

The unit consisted of a batch, stirred, stainless steel reactor (12 L), a vapour cooling section (reflux cooler), a vacuum pump as well as systems for collecting the liquid and gas samples and temperature/pressure/energy consumption controllers and recorders. The stirrer is designed with such a geometry in order to homogenize efficiently liquid/solid or solid/solid mixtures, giving a circular and upward direction to the components of the mixture. In order to prevent gases from contaminating the vacuum pump, a cold trap containing liquid nitrogen was added after the vapour cooling section and before the vacuum pump. In the second reactor configuration, a fixed bed catalytic vapour upgrading section was added into the reactor, so that produced vapours could pass through it before they exit the reactor system.

Figure 3-1. (a) Reactor, (b) stirring device and (c) vapour condensation section

The flowsheet of the reactor system is presented below:

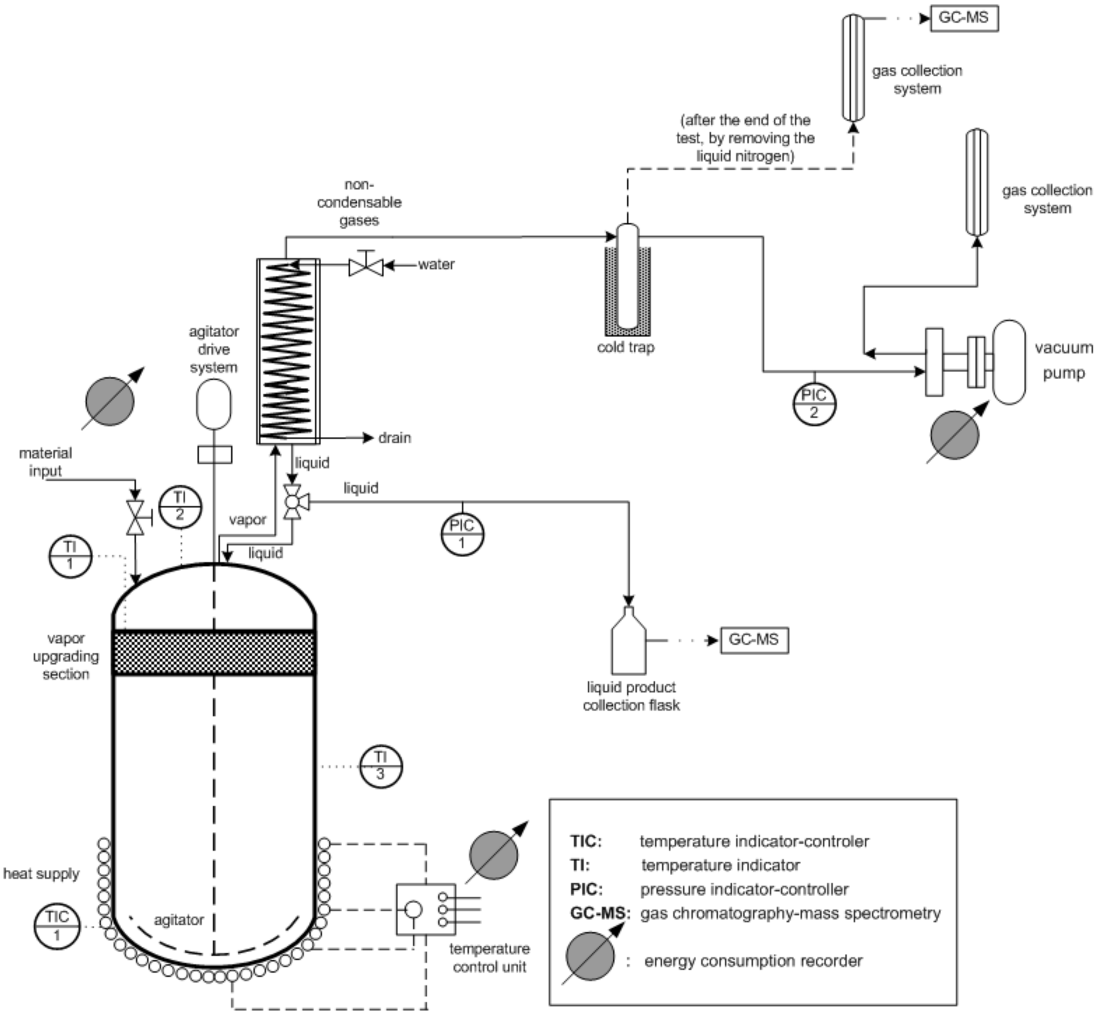


Figure 3-2. The reactor system

3.3.2 Experimental procedure

Before each test, the biogenic feedstock was dried (humidity <10% wt.), milled and sieved (0,500mm-1,000mm). The catalyst was activated in the muffle oven at 500 ℃ for 1h, in order to release any water absorbed into its pores.

Non-catalytic and catalytic tests with three different types of catalysts were performed. The biomass (500 g), the liquid carrier (1 L) or the inert solid carrier (1500 g) and the catalyst (15 g) were mixed and fed into the reactor. In the case when the vapour upgrading section was used, catalyst (50 g) was also added in the section. The reactant system was sealed and the oxygen was removed from the system.

The temperature was set and controlled through a temperature control system. During the experiments, the pressure was controlled and set at slight vacuum (0.9 bar). The final reaction temperature used for the presented experiments was 350 ℃ and 400 ℃ and a heating rate of ~6 ℃/min was used. The parameters of the process were selected to achieve the highest conversion of biomass to liquid products at relatively mild conditions that could increase the energy efficiency of the process. The mixture was vigorously stirred during the test. The produced vapours exited the reactor, due to the slight vacuum applied into the system. They were condensed at the vapour cooling section and collected in the liquid products' flask. The non-condensable gases exited the vapour cooling section and were trapped in the cold trap. Gases that were non-condensable in the cold trap exited the system via the vacuum pump and were guided into a gas collection system. The experimental apparatus was held at the final temperature until no further significant release of vapours was observed. After the end of the test, the cold trap was isolated from the system, the liquid nitrogen was removed and the gases were guided into a gas collection system.

The liquid product contained of two easily separated phases: a lighter organic and a heavier aqueous phase. The two phases are left to stand still into a decanter and then they are easily separated due to their different density. Samples of the collected gas, the organic and the aqueous phases and the residue are sent for physicochemical analysis.

3.3.3 Analysis of products

After the end of the experiment, the liquid products and the residues were weighed, while the gas products were measured volumetrically. The liquid and gas products were analyzed with the help of an Agilent 6890N Gas Chromatographer equipped with a 5973 Mass Selective Detector. The compounds were identified using the Wiley 275 library. For the liquid samples (organic and aqueous phases), the separation was performed on a HP5-MS column (Agilent Technologies) with (5% phenyl)methyl-polysiloxane layer (30 m x 0.25 mm i.d. x 0.25 µm film thickness) with the aid of helium as a carrier gas (0.3 mL/min). The inlet temperature was set at 240 ℃ (split ration 20:1) while the oven temperature started at 40 ℃ with a gradient of 5 ℃/min to 300 ℃ where the temperature was held for 2 min. The injection volume was 1 µL. For the gas samples, the separation was performed on a GS-GASPRO column (Agilent Technologies) (60 m x 0.324 mm i.d.) using helium as a carrier gas (3.3 mL/min). The inlet temperature was set at 60 ℃ (split ratio 1:17) while the oven temperature was 80 ℃ for 0.5 min, then increased to 175 ℃ with a gradient of 25 ℃/min, and was held at this temperature value for 2 min. Afterwards, an increase with a gradient of 25 ℃/min followed until 250 ℃. The injection volume was 500 µL (manual injection with a gas tight syringe).

The C and H contents were determined on a Universal CHN Elemental Analyzer Vario El. The sulfur contents were assessed by UV-fluorescence detection on a Mitsubishi TS-100 Analyzer. Dibutylsulfide in toluene was used for the trace level calibration. Furthermore, nitrogen determination was performed on the same apparatus but via chemiluminescence detection. The calibration was performed with pyridine. Finally, the oxide ash was measured in accordance with DIN EN ISO 6245, after heating a sample at a muffle furnace at 775 ℃ for 20–30 min and weighing, then repeating until consecutive weightings differed no more than 0.5 mg.

The water content in liquid phases was measured by the Karl– Fischer titration on an 808 Titrando (Metrohm AG). The attained data were evaluated with the aid of the Tiamo 1.1 software. The density and viscosity measurements were carried out by the SVM 300 Stabinger Viscometer (Anton Paar Ltd.). The water content in the biomass was determined by drying at 120 ℃ for 24 h.

3.3.4 Catalyst regeneration and characterization

The spent zeolites, from both the reactor and the vapour upgrading section, were regenerated in a muffle oven at 500 ℃ for 24 h to remove all the coke from the zeolite structure. The structure and phase purity of the zeolites were studied by X-ray powder diffraction (XRD). The sample of the regenerated zeolite was milled and the fine powder was pressed on a sample holder. The main structural components were identified by X-ray diffraction analysis (Panalytical XPert Pro) in the angle range between 4° and 110° 2θ CoKα. The evaluation of the X-ray diffractograms was performed by means of the Panalytical Software XPert Highscore Plus and database PDF-2 (Release 2007).

3.3 SELECTION OF FEEDSTOCKS

The present research focused on the utilization of feedstocks with low edible-use, such as organic wastes and aquatic plants. The following biogenic feedstocks were selected for experimental testing:

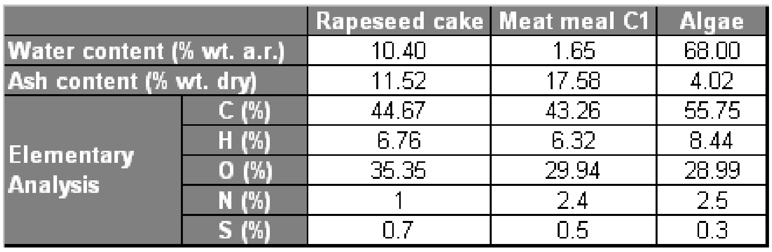
(a) Rapeseed cake: a large amount of rapeseed cake is obtained as a by-product from rapeseed oil production by the press and extraction method. The properties of the cake depend on the type of rapeseed plant, for instance canola can be used as cattle-feed (Özçimen and Karaosmanoğlu, 2004). For other types of rapeseed cake, their utilization through the production of liquid fuels would increase the total liquid fuel yield of the biodiesel production. The rapeseed cake used in the performed tests was obtained via the mechanical cold press extraction method at BioDiesel Kaernten, in the area of Carinthia, Austria.

(b) Meat meal C1: meat meal is prepared by the organic residues associated with slaughtering processes and rendering of dead animals. Its composition can vary, depending on the materials used and their blending. Category C1 comprises of animal by-products of high health risk, due to infection with communicable illnesses, viruses or exposure to other pharmaceutical substances. Due to the fact that pathogenic organisms have been detected to meat meal C1, now it's usually incinerated instead of being used as animal feed. Recently, the use of meat meal for biodiesel production has been allowed. Its use for the production of biofuels and biochemicals could also be explored. The meat meal C1 used in the performed tests was supplied by the a waste collection company in Slovenia.

(c) Algae: algae are aquatic plants, which grow in both fresh and salty water and show a high production rate and high productivity. Algae appear to have a good potential for their use in biofuel and biochemical production. The algae used in the performed tests were supplied from Jakobs University in Germany.

The physicochemical properties of the selected materials are presented in the following Table:

Table 3-1: Physicochemical properties overview of the selected solid biogenic materials



		Rapeseed cake	Meat meal C1	Algae
Water content (% wt. a.r.)		10.40	1.65	68.00
Ash content (% wt. dry)		11.52	17.58	4.02
Elementary Analysis	**C (%)**	44.67	43.26	55.75
	H (%)	6.76	6.32	8.44
	O (%)	35.35	29.94	28.99
	N (%)	1	2.4	2.5
	S (%)	0.7	0.5	0.3

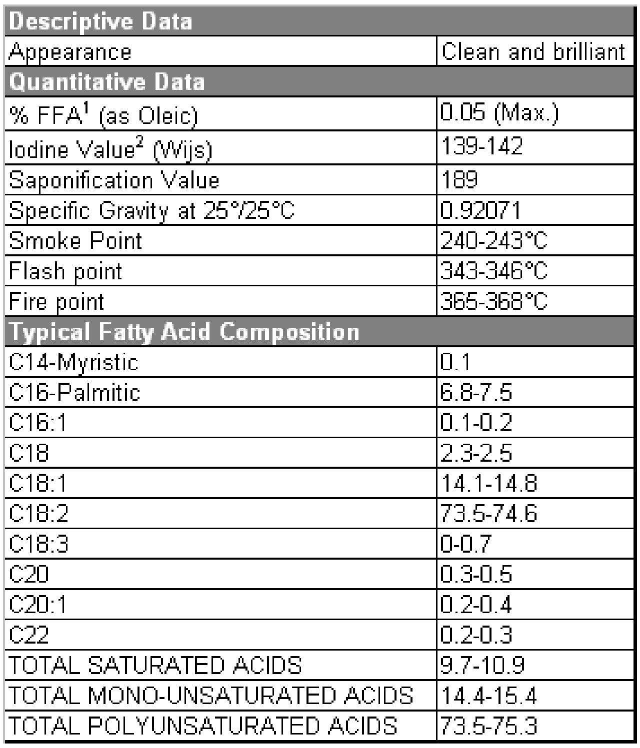
3.4 SELECTION OF LIQUID CARRIER / SOLID CARRIER MATERIAL

During the biomass conversion tests, the carrier material can either act as a heat carrier or/and as a promoter of chemical reactions to produce liquid products of higher added value. In the first case, it can stay inert during the biomass conversion, in the second case it will be consumed during the reaction. If the carrier is in the liquid state, it should have a high boiling point, since the KNV process runs at slight vacuum. The high temperature range of the KNV process requires a liquid carrier with low toxicity, low corrosiveness, high flame point and high thermochemical stability.

For the performed tests, vegetable oils were selected to be tested as liquid carriers, due to their bio-based nature, in contrast to other used liquid carriers, such as tetralin or vacuum gasoil. As fatty oil, the linoleic type of safflower oil (rich in esters of polyunsaturated fatty acids) was used, supplied by the food company Estermann (Austria).

The physicochemical properties of the safflower oil are summarized in the following Table:

Table 3-2: Physicochemical properties overview of the safflower oil



Descriptive Data	
Appearance	Clean and brilliant
Quantitative Data	
% FFA^1 (as Oleic)	0.05 (Max.)
Iodine Value^2 (Wijs)	139-142
Saponification Value	189
Specific Gravity at 25°/25°C	0.92071
Smoke Point	240-243°C
Flash point	343-346°C
Fire point	365-368°C
Typical Fatty Acid Composition	
C14-Myristic	0.1
C16-Palmitic	6.8-7.5
C16:1	0.1-0.2
C18	2.3-2.5
C18:1	14.1-14.8
C18:2	73.5-74.6
C18:3	0-0.7
C20	0.3-0.5
C20:1	0.2-0.4
C22	0.2-0.3
TOTAL SATURATED ACIDS	9.7-10.9
TOTAL MONO-UNSATURATED ACIDS	14.4-15.4
TOTAL POLYUNSATURATED ACIDS	73.5-75.3

Quartz sand was selected as a solid carrier material, since it consists of >90% SiO_2, it is chemically stable until 2230 ℃ and it is highly resistant to attrition. The quarz sand was supplied by the company Quarzwerke (Austria).

3.5 SELECTION OF CATALYSTS

Three different types of zeolite catalysts were used for the experiments: (1) Fe-ZSM-5 (SiO_2/Al_2O_3 molar ratio: 27), (2) H-ZSM-5 (SiO_2/Al_2O_3 molar ratio: 27) and (3) H-Beta (SiO_2/Al_2O_3 molar ratio: 25). The catalysts were produced by SüdChemie AG. Their physicochemical properties are presented in the following Table:

Table 3-3: Physicochemical properties of the zeolites used for the KNV experiments (Süd-Chemie, 2006)

Analysis		H-MFI-27 P	Fe-MFI-27 P	H-BEA-25 P
Loss on Ignition	(wt%)	5,39	7	12,6
Si	(wt%)	44,69	38,2	37,7
Al	(wt%)	3,54	3,2	3,09
Fe_2O_3	(wt%)	-	3,5	-
Na_2O	(wt%)	0,02	0	0,004
Langmuir Surface Area	(m^2/g)	414	363	564
Laser Sizing: d_{50}	(µm)	11,9	7,5	4,9

The three zeolite catalysts possess particular characteristics: H-Beta is an acidic catalyst with wide pores, H-ZSM-5 has strong acidic properties and small pores and Fe-ZSM-5 is a mild solid acid containing a transition metal.

Zeolite ZSM-5 catalysts have a strong acidity, high activities and shape selectivities, which can convert the oxygenated bio-oil to light hydrocarbons C1–C10 by dehydration and deoxygenation reactions (Williams and Horne, 1995). The effect of shape-selectivity is still enhanced with the hydrogen exchange in ZSM-5 zeolite with bigger Fe^{3+} cations. In addition, the Fe exchanged form of ZSM-5 zeolite has a lower total acidity at the absence of very strong acidic sites compared with H-ZSM-5 zeolite (Das et al., 1995). The presence of Fe can promote metal catalyzed reactions, such as hydrogenation. Zeolite Beta catalysts have a medium acidity and larger pore size than zeolite ZSM-5, which makes easier the access to active sites, located inside its pores, for large molecules of biomass origin.

3.6 PERFORMED TESTS / RESULTS

3.6.1 CO-CONVERSION OF RAPESEED CAKE AND SAFFLOWER OIL

3.6.1.1 SCIENTIFIC BACKGROUND

Rapeseed oil is one of the most important sources not only for the edible-oil technology, but also for the biodiesel production. A large rapeseed cake amount is obtained as a by-product of rapeseed oil production. The increased production of the rapeseed cake as a by-product reduces its demand. Therefore, it has to be converted efficiently into a high added value product to help the economics of biodiesel production plants. Safflower oil is a widely used vegetable oil for edible and non-edible purposes, e.g. biodiesel production.

The catalytic pyrolysis of vegetable oils, used vegetable oils and fatty acids has also been previously studied. Different types of zeolites had been used, such as ZSM-5, Beta, MCM-41, SBA-15 and REY (Alencar et al., 1983; Chew and Bhatia, 2008; Huber and Corma, 2007; Leung et al., 1995; Lima et al., 2004). Zeolites demonstrated a very good performance as solid acid cracking catalysts, owing to their material properties. Results showed that a gasoline-like or diesel-like fuel could be produced.

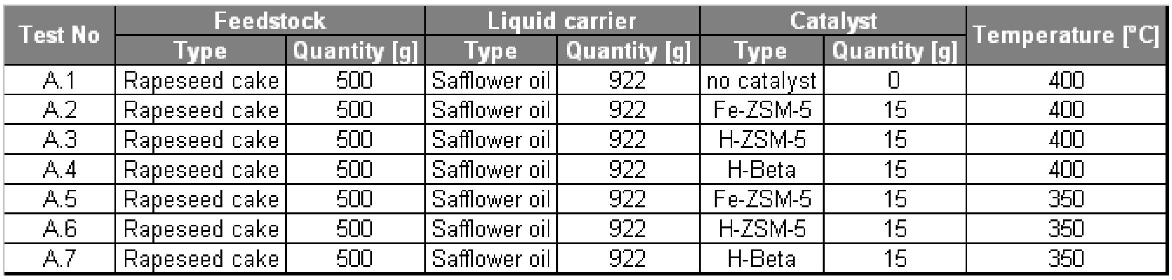
All biomass fuels have potential to significantly reduce the import of petroleum products. Additionally, economies of scale can play a large factor in lowering the product cost. Therefore, opportunities to co-feed with coal or natural gas systems may be one way to get renewable fuels into the marketplace, just as co-firing biomass with coal is being done in the power generation industry (Spath and Dayton, 2003).

The co-processing of these feedstocks is an interesting approach in terms of material efficiency and economics. Low pressure conversion can give the possibility to better regulate the residence time of produced vapours into the reactor system, enabling the increase of liquid product yield without the use of high-investment reactors, e.g. fluidized bed. The catalyst addition into the reactor system is expected to improve the quality of the liquid product by promoting the formation of compounds with high added value and less oxygen content.

3.6.1.2 PERFORMED TESTS

The following tests were performed (set of tests: A):

Table 3-4: Performed tests overview of the rapeseed cake and safflower oil co-conversion



Test No	Feedstock		Liquid carrier		Catalyst		Temperature [°C]
	Type	Quantity [g]	Type	Quantity [g]	Type	Quantity [g]	
A.1	Rapeseed cake	500	Safflower oil	922	no catalyst	0	400
A.2	Rapeseed cake	500	Safflower oil	922	Fe-ZSM-5	15	400
A.3	Rapeseed cake	500	Safflower oil	922	H-ZSM-5	15	400
A.4	Rapeseed cake	500	Safflower oil	922	H-Beta	15	400
A.5	Rapeseed cake	500	Safflower oil	922	Fe-ZSM-5	15	350
A.6	Rapeseed cake	500	Safflower oil	922	H-ZSM-5	15	350
A.7	Rapeseed cake	500	Safflower oil	922	H-Beta	15	350

3.6.1.3 PHASE COMPOSITION OF THE REACTION MIXTURE

In each experiment the mixture of the liquid product, the solid residue and the gases was obtained. The liquid products consisted of two well separated phases: an organic and an aqueous phase. The relative contents of these phases depended on the process temperature and the catalyst used:

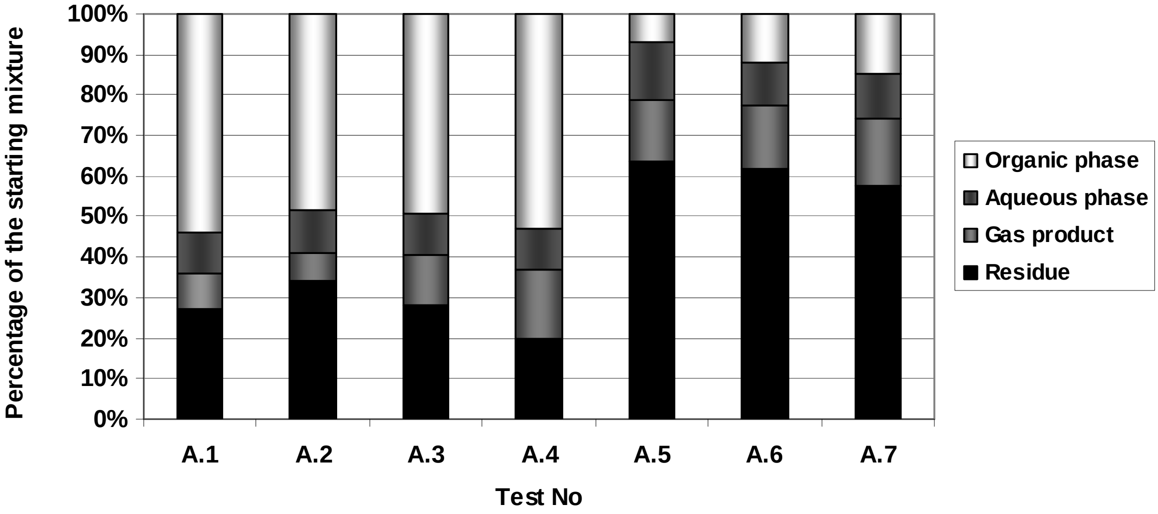


Figure 3-3. Product yields (wt. % on biogenic mixture) of the performed rapeseed cake and safflower oil co-conversion tests

At 400 ℃, the non-catalytic run exhibited the highest liquid product yield compared with that of all catalytic runs. A low gas product yield was formed at the absence of the catalysts. Deep cracking leads to the formation of gas products.

At both process temperatures, the H-Beta zeolite displayed the lowest residue production and the highest liquid production, while the Fe-ZSM-5 zeolite presented the highest residue production and the lowest liquid production. At 350 ℃, the liquid phase yield was significantly decreased. In addition, a considerable residue amount was formed at these conditions.

At 400 ℃, the organic liquid phase yield was the highest after the non-catalytic test. For the catalytic tests, H-Beta resulted in its higher formation. In reference with the aqueous phases, their yields slightly depended on the catalyst. On the contrary, at 350 ℃, the organic phase yields increased by the following order: Fe-ZSM-5 < H-ZSM-5 < H-Beta, while for the aqueous phase yield this order was reversed: H-Beta ≃ H-ZSM-5 < Fe-ZSM-5.

At both temperatures, CO_2 and light hydrocarbons (C2-C6) were present in the gas phases.

3.6.1.4 CHEMICAL COMPOSITION OF THE ORGANIC PHASE

The chemical composition of the organic phases, gained at different tests, is depicted in the following Figure. The components are classified into chemical groups according to their chemical structure. The individual compounds found in organic phases (with their contents) are listed in Table 8-5 in the Annex.

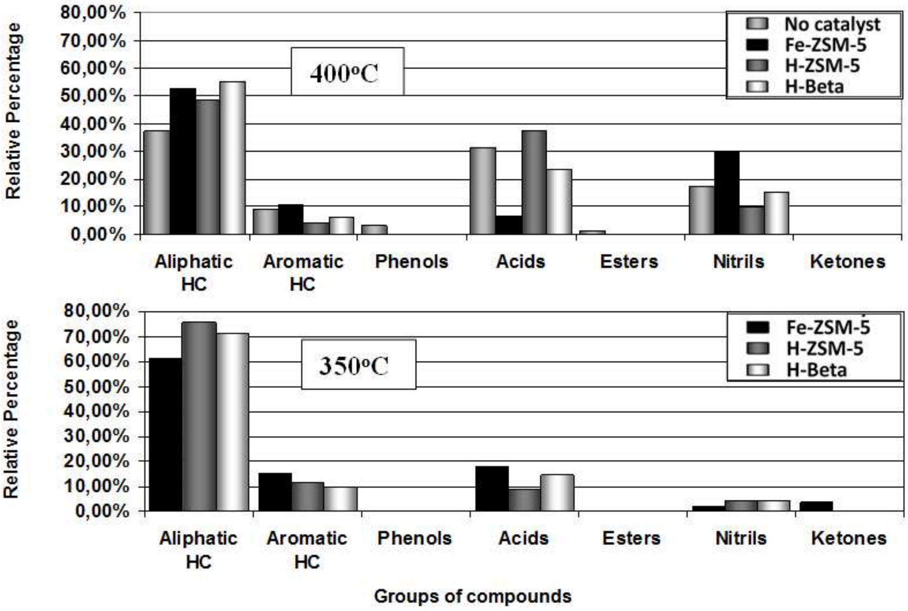


Figure 3-4. Organic phase composition of the rapeseed cake and safflower oil co-conversion liquid products

At 400 °C, the non-catalytic conversion of feedstock led to low yields of aliphatic hydrocarbons, being essential components of the fuel. In contrast, the liquid phase, obtained after the catalytic conversion, became rich on compounds of this group. As to the aromatic hydrocarbons, the Fe-ZSM-5 zeolite slightly increased their yield, while the H-forms of zeolites reduced it. The total yield of hydrocarbons (aliphatic and aromatic) was higher for the Fe-ZSM-5 and H-Beta zeolites (~63%).

As it can be seen in Figure 3-4, the remaining fatty acid contents were the lowest after the conversion on Fe-ZSM-5 zeolite (~6%). At the same time, the yield of hydrocarbons and nitriles was the highest.

Conducting the experiments at lower temperature significantly changed the organic phase composition. The contents of the aliphatic and aromatic hydrocarbons were higher at significantly reduced amount of fatty acids and nitriles. The summary contents of all hydrocarbons were higher for the H-ZSM-5 zeolite (~85%). The Fe-ZSM-5 zeolite demonstrated a higher production of aromatic hydrocarbons. Finally, at this temperature, a very low amount of nitriles was found in the reaction mixture.

3.6.1.5 CHEMICAL COMPOSITION OF THE AQUEOUS PHASE

The aqueous phase analysis illustrated the presence of the following groups of water-soluble compounds: carboxylic acids and their derivatives (esters, nitriles), phenols, heterocyclic compounds, alcohols, aldehydes and ketones (Figure 3-5). Among these products all catalysts favored the formation of short-chain acids and N-heterocyclic compounds.

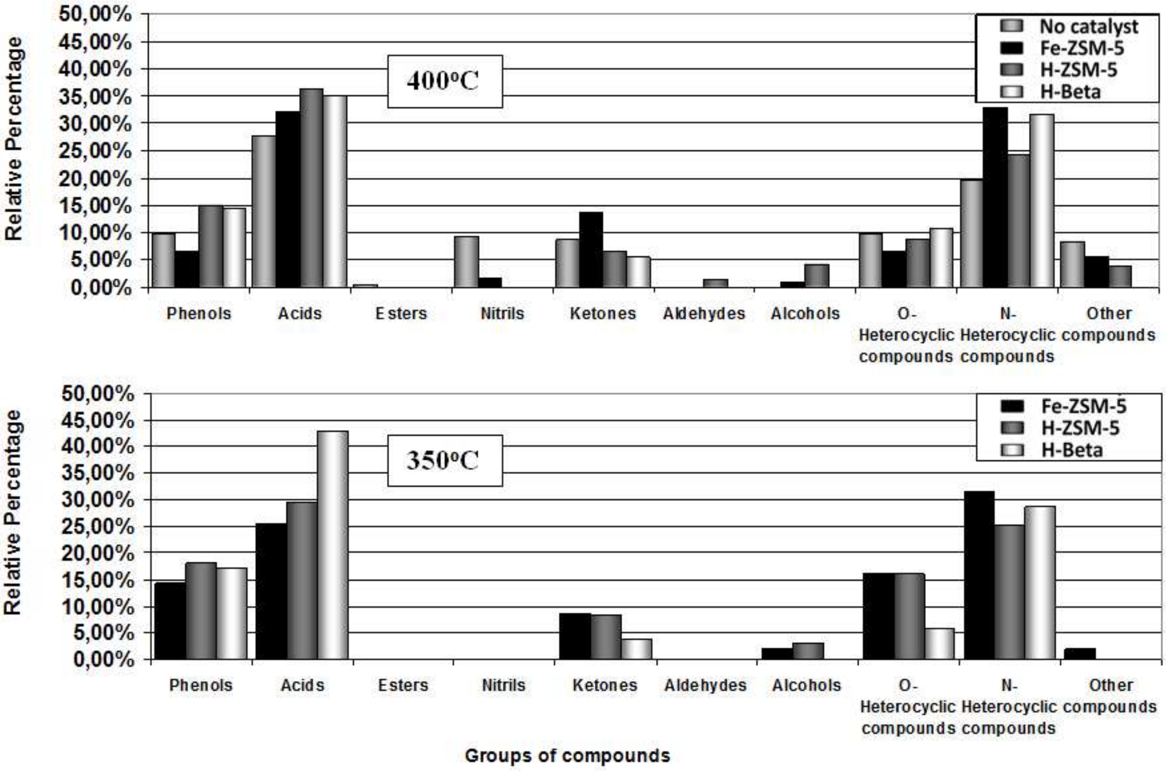


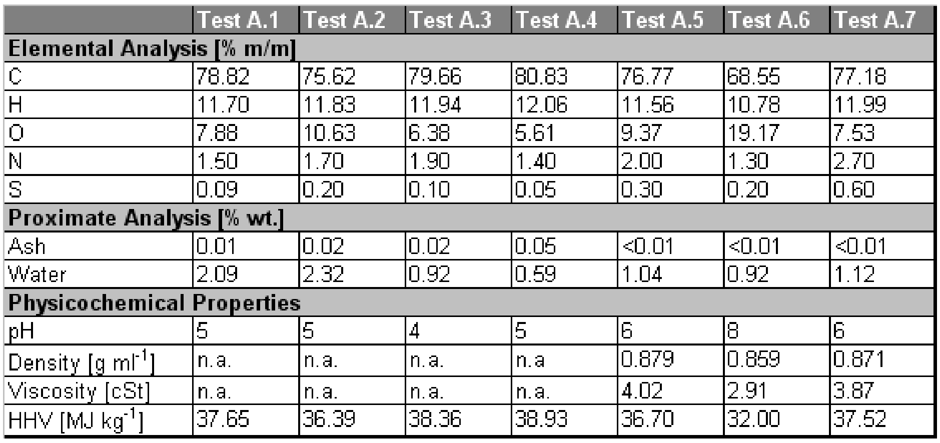
Figure 3-5. Aqueous phase composition of the rapeseed cake and safflower co-conversion liquid products

At 400 ℃, the highest yields of short-chain acids were observed at the H-ZSM-5 and H-Beta zeolites and the lowest at the non-catalytic test. The yield of the phenolic compounds was higher on the H-ZSM-5 and H-Beta zeolites and very low when Fe-ZSM-5 was applied. The O-heterocyclic compound production was insignificantly dependent on the absence or presence of different catalyst type. Finally, comparing the catalytic runs, the N-heterocyclic compound production was the lowest when the H-ZSM-5 zeolite was used. The distribution of the water-soluble products by the groups was almost similar at both experimental temperature values. However, at 350 °C the acid formation on H-Beta zeolite was significantly higher than that on other catalysts.

3.6.1.6 ELEMENTAL COMPOSITION / PHYSICAL PROPERTIES

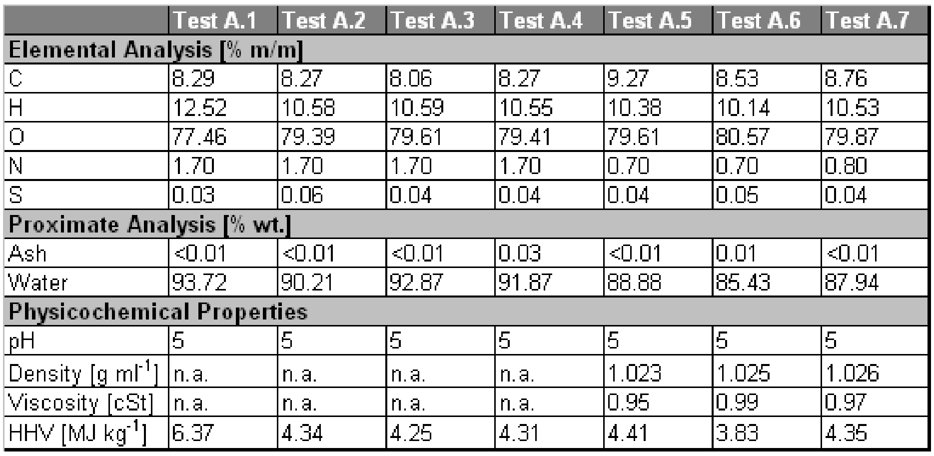
The elemental composition results and the physical properties of the produced organic phase, aqueous phase and residue are depicted in the following Tables:

Table 3-5: Organic phase characteristics of the rapeseed cake and safflower oil co-conversion tests



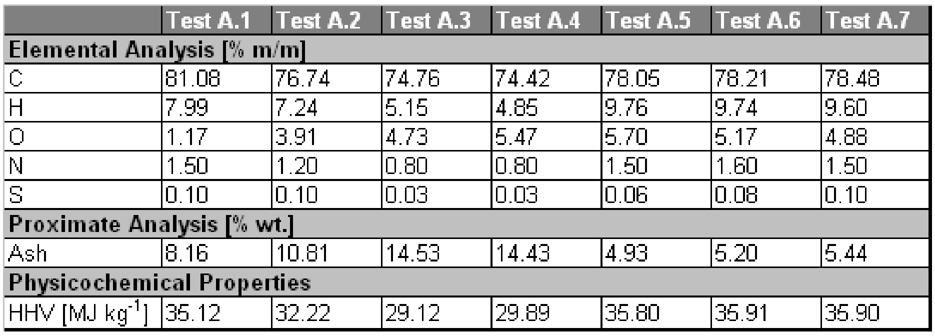
	Test A.1	Test A.2	Test A.3	Test A.4	Test A.5	Test A.6	Test A.7
Elemental Analysis [% m/m]							
C	78.82	75.62	79.66	80.83	76.77	68.55	77.18
H	11.70	11.83	11.94	12.06	11.56	10.78	11.99
O	7.88	10.63	6.38	5.61	9.37	19.17	7.53
N	1.50	1.70	1.90	1.40	2.00	1.30	2.70
S	0.09	0.20	0.10	0.05	0.30	0.20	0.60
Proximate Analysis [% wt.]							
Ash	0.01	0.02	0.02	0.05	<0.01	<0.01	<0.01
Water	2.09	2.32	0.92	0.59	1.04	0.92	1.12
Physicochemical Properties							
pH	5	5	4	5	6	8	6
Density [g ml^{-1}]	n.a.	n.a.	n.a.	n.a	0.879	0.859	0.871
Viscosity [cSt]	n.a.	n.a.	n.a.	n.a.	4.02	2.91	3.87
HHV [MJ kg^{-1}]	37.65	36.39	38.36	38.93	36.70	32.00	37.52

Table 3-6: Aqueous phase characteristics of the rapeseed cake and safflower oil co-conversion tests



	Test A.1	Test A.2	Test A.3	Test A.4	Test A.5	Test A.6	Test A.7
Elemental Analysis [% m/m]							
C	8.29	8.27	8.06	8.27	9.27	8.53	8.76
H	12.52	10.58	10.59	10.55	10.38	10.14	10.53
O	77.46	79.39	79.61	79.41	79.61	80.57	79.87
N	1.70	1.70	1.70	1.70	0.70	0.70	0.80
S	0.03	0.06	0.04	0.04	0.04	0.05	0.04
Proximate Analysis [% wt.]							
Ash	<0.01	<0.01	<0.01	0.03	<0.01	0.01	<0.01
Water	93.72	90.21	92.87	91.87	88.88	85.43	87.94
Physicochemical Properties							
pH	5	5	5	5	5	5	5
Density [g ml^{-1}]	n.a.	n.a.	n.a.	n.a.	1.023	1.025	1.026
Viscosity [cSt]	n.a.	n.a.	n.a.	n.a.	0.95	0.99	0.97
HHV [MJ kg^{-1}]	6.37	4.34	4.25	4.31	4.41	3.83	4.35

Table 3-7: Residue characteristics of the rapeseed cake and safflower oil co-conversion tests



	Test A.1	Test A.2	Test A.3	Test A.4	Test A.5	Test A.6	Test A.7
Elemental Analysis [% m/m]							
C	81.08	76.74	74.76	74.42	78.05	78.21	78.48
H	7.99	7.24	5.15	4.85	9.76	9.74	9.60
O	1.17	3.91	4.73	5.47	5.70	5.17	4.88
N	1.50	1.20	0.80	0.80	1.50	1.60	1.50
S	0.10	0.10	0.03	0.03	0.06	0.08	0.10
Proximate Analysis [% wt.]							
Ash	8.16	10.81	14.53	14.43	4.93	5.20	5.44
Physicochemical Properties							
HHV [MJ kg^{-1}]	35.12	32.22	29.12	29.89	35.80	35.91	35.90

Comparing the elemental analysis data, it's obvious that the organic phase produced on the H-Beta zeolite demonstrated the lowest oxygen content. Sulfur is another undesirable component of fuels. Sulfur content in the organic phases was low in comparison with No. 4 fuel oil and No. 6 fuel oil (according to the classification with the U.S. nomenclature) (1.5-4.0% wt.) (Özçimen and Karaosmanoğlu, 2004). Among the catalysts, at 400 °C the H-Beta zeolite provided the lowest sulfur contents.

The water content in all organic phases was low in comparison with that of the pyrolysis bio-oil (Bridgwater, 1994). At 400 °C, the water content decreased by the following order: Fe-ZSM-5 > H-ZSM-5 > H-Beta. At 350 °C, the water content of the organic phases was approximately similar on all catalysts. The pH value of organic phases was higher than the pH of typical wood pyrolysis oil (2-2.5) (Bridgwater, 1994), making it easier to handle due to reduced corrosion effect.

The produced organic phases possessed higher Higher Heating Values (HHV) than pyrolysis and liquefaction oils (19.3 and 30-35 MJ/kg respectively) (Bridgwater 1994; Naber et al., 2002). At 350 °C, the densities and viscosities of the organic phases were similar to that of diesel (~0.85 g ml^{-1} and 2-4.5 cSt respectively).

As shown in Table 3-7, at 400 °C, the HHV of residues decreased by the following order: non-catalytic > Fe-ZSM-5 > H-ZSM-5 ≃ H-Beta. At 350 °C, the HHV of residues from all tests was similar.

3.6.2 RAPESEED CAKE CONVERSION WITH TWO REACTOR CONFIGURATIONS

3.6.2.1 SCIENTIFIC BACKGROUND

The catalytic upgrading of bio-oils can be performed in situ in specially designed reactor systems, by mixing the biogenic feedstocks with the catalysts (Adam et al., 2006; Aho et al., 2008; Antonakou et al., 2006a; Antonakou et al., 2006b; Demiral and Şensöz, 2008; Pütün et al., 2006; Williams and Nugranad, 2000; Zhang et al., 2009). Alternatively, it can be performed in series with the thermochemical process (Gayubo et al., 2005; Vitolo et al., 1999; Vitolo et al., 2001), by evapourating the produced bio-oil and bringing it in contact with the upgrading catalyst, including a costly vapour condensation/re-evapouration step.

The presence of a significant water amount in the liquid products can affect the structure and acidic properties of the zeolite catalysts. The hydrothermal treatment of ZSM-5 and Beta zeolites causes the migration of tetrahedral framework Al to extraframework positions, where it is positively charged (Cejka et al., 1995; Fan et al., 2006; Kuehl and Timken, 2000). As a result, new strong Lewis acid sites are formed in the material, while the number of Brønsted acid sites is reduced (Fan et al., 2006). The extraframework Al is active in coke formation (Cejka et al., 1995). The accumulation of extraframework Al at the outer surface of zeolite crystals reduces the material pore size. Therefore, steric hindrances are created during catalytic reactions (Fan et al., 2006). It has been reported that the number of stronger acid sites of ZSM-5 zeolites decreased in increasing steaming time (Masuda et al., 1998). The steamed ZSM-5 zeolites do not appear to have a degraded crystalline structure compared with the parent material (Cejka et al., 1995; Fan et al., 2006). The Beta zeolite contains a substantial concentration of lattice defects (Kuehl and Timken, 2000). When the Beta zeolite is steamed, the micropore structure remains intact. However, the intense steaming of the Beta zeolite creates clefts or mesopores in zeolite crystallites, shortening the diffusion pathways to the framework active sites (Van Bokhoven et al., 2002).

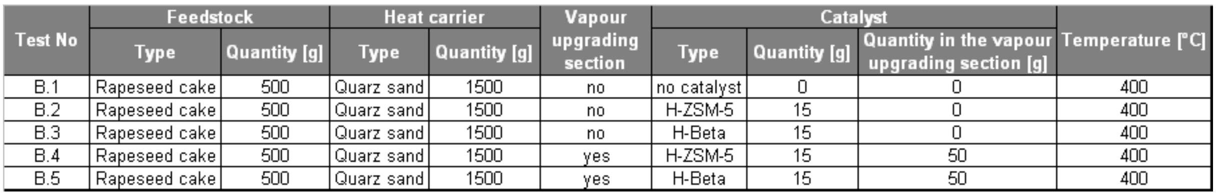
The subsequent citric acid treatment of the ZSM-5 zeolite can have as an effect the zeolite realumination. Unlike ZSM-5, the Beta zeolite can be realuminated by citric acid without prior steaming (Fan et al., 2006). It has also been reported that octahedrally coordinated Al species of the Beta zeolite can reversibly convert to tetrahedral Al sites upon reaction with NH_3 gas (Kuehl and Timken, 2000). When Beta zeolite is steamed and then treated with NH_3, the octahedral Al reverts to tetrahedral, but part of the fine structure is lost. It indicates a loss or ordering around some of the Al atoms and the formation of an amorphous phase, probably silica-alumina (Van Bokhoven et al., 2002).

In the case of the ZSM-5 zeolite, a considerable portion of Lewis acid sites is in pseudo-tetrahedral symmetry. In the case of the Beta zeolite, the Lewis acid sites are predominantly in octahedral symmetry, probably due to the larger pore volume of the Beta zeolite, allowing enough space for the coordination of Al with three water molecules (Kuehl and Timken, 2000).

3.6.2.2 PERFORMED TESTS

The following tests were performed (set of tests: B):

Table 3-8: Performed tests overview of the rapeseed cake conversion using two reactor configurations



Test No	Feedstock		Heat carrier		Vapour upgrading section	Catalyst			Temperature [°C]
	Type	Quantity [g]	Type	Quantity [g]		Type	Quantity [g]	Quantity in the vapour upgrading section [g]	
B.1	Rapeseed cake	500	Quarz sand	1500	no	no catalyst	0	0	400
B.2	Rapeseed cake	500	Quarz sand	1500	no	H-ZSM-5	15	0	400
B.3	Rapeseed cake	500	Quarz sand	1500	no	H-Beta	15	0	400
B.4	Rapeseed cake	500	Quarz sand	1500	yes	H-ZSM-5	15	50	400
B.5	Rapeseed cake	500	Quarz sand	1500	yes	H-Beta	15	50	400

3.6.2.3 PHASE COMPOSITION OF THE REACTION MIXTURE

In each experiment the mixture of the organic liquid phase, the aqueous liquid phase, the solid residue and the gases were obtained. The liquid products consisted of two well separated phases: an organic and an aqueous phase. The relative contents of these phases depended on the reactor configuration and the used catalyst (Figure 3-6).

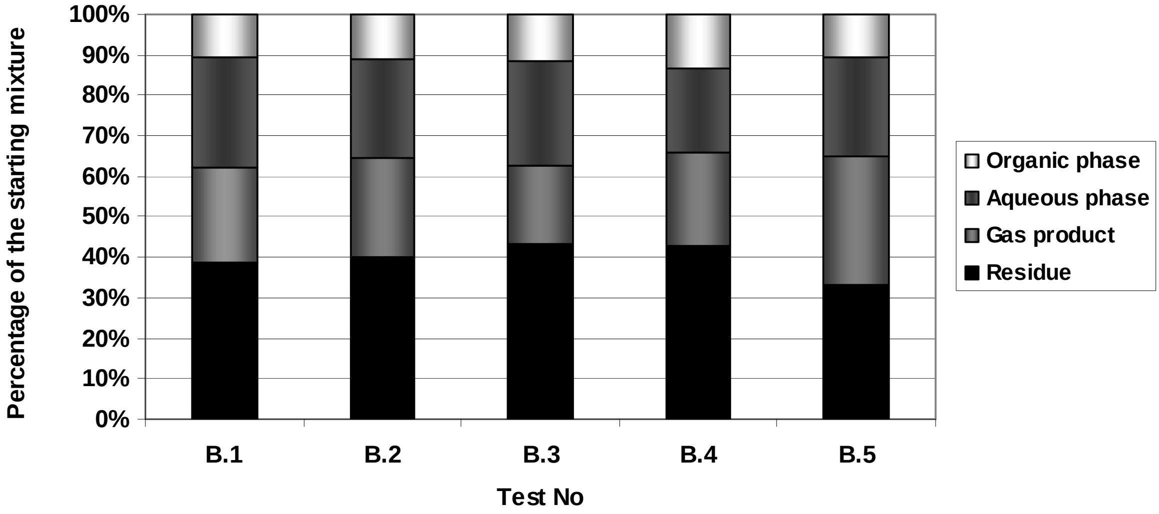


Figure 3-6. Product yields (wt. % on biogenic mixture) of the performed rapeseed cake conversion tests using two reactor configurations

The liquid product yields decreased by the following order: non catalytic ≃ H-Beta > H-ZSM-5 > H-Beta (upgr.) > H-ZSM-5 (upgr.). As it has already been mentioned, the catalytic biomass conversion tests usually result in a lower liquid product yield compared with non-catalytic one.

In the absence of the vapour upgrading section, the H-ZSM-5 zeolite showed better catalytic activity, since it produced less residue and more gas products than the H-Beta zeolite. However, in the presence of the vapour upgrading section, the H-Beta zeolite was more active than H-ZSM-5, gaining the lowest residue yield and the highest gas product yield.

The organic phase production increased by the following order: H-ZSM-5 (upgr.) > H-Beta > H-ZSM-5 > non catalytic > H-Beta (upgr.).

CO_2 and light hydrocarbons (C2-C6) were present in the gas phases.

3.6.2.4 CHEMICAL COMPOSITION OF THE ORGANIC PHASE

The chemical composition of the organic phases, gained at different tests, is depicted in the following Figure. The components are classified into chemical groups according to their chemical structure. The individual compounds found in organic phases (with their contents) are listed in Table 8-7 in the Annex.

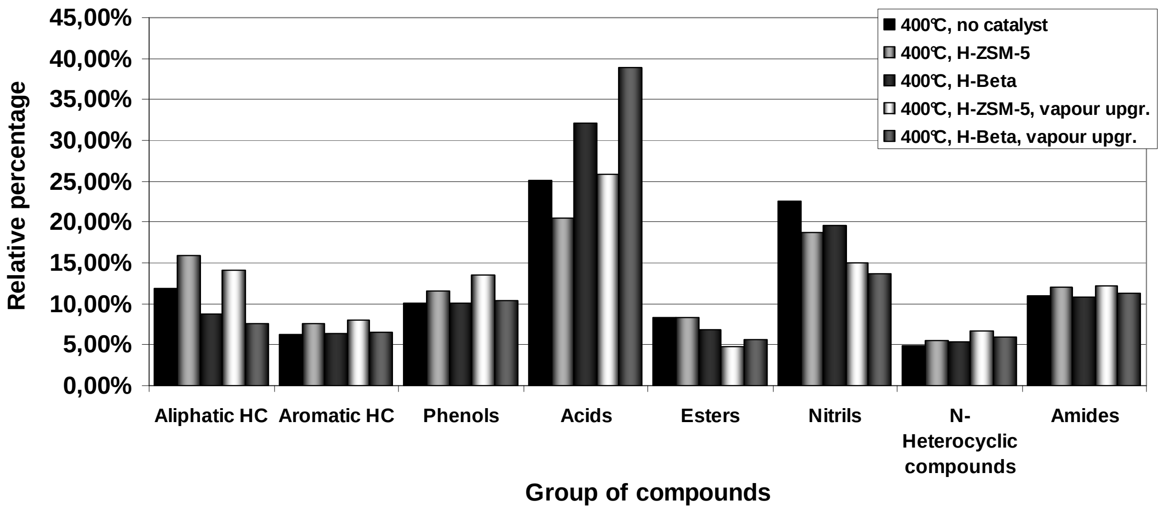


Figure 3-7. Organic phase composition of the rapeseed cake conversion liquid products using two reactor configurations

As shown in Figure 3-7, the major organic phase components were carboxylic acids and their derivatives: esters, amides and nitriles. The acid yields on the H-Beta zeolite were higher than on H-ZSM-5. In the presence of the vapour upgrading section their yields increased. In contrast, the ester and nitrile yields decreased with the vapour upgrading section. The ester and nitrile production was maximized at the non-catalytic test. The yields of amides, that are the intermediate products of acid conversion into nitriles, are almost independent on the catalyst. The presence of the vapour upgrading section slightly reduced their yields.

Hydrocarbons are another large group of compounds. Their maximum yield was attained on the H-ZSM-5 zeolite and a slightly reduced yield on the H-Beta zeolite. The use of the vapour upgrading section with both catalysts reduced the aliphatic and aromatic hydrocarbon yields. In all cases, the aliphatic hydrocarbon production prevailed over the aromatic ones.

The H-Beta zeolite was less active in the phenol production than H-ZSM-5 zeolite. The use of H-ZSM-5 zeolite and the vapour upgrading section reduced the phenol yield. No clear dependence was found between the vapour upgrading and the N-heterocyclic compound yields.

3.6.2.5 CHEMICAL COMPOSITION OF THE AQUEOUS PHASE

The aqueous phase analysis showed the presence of the following groups of water-soluble compounds: phenols, heterocyclic compounds, alcohols and ketones (Figure 3-8).

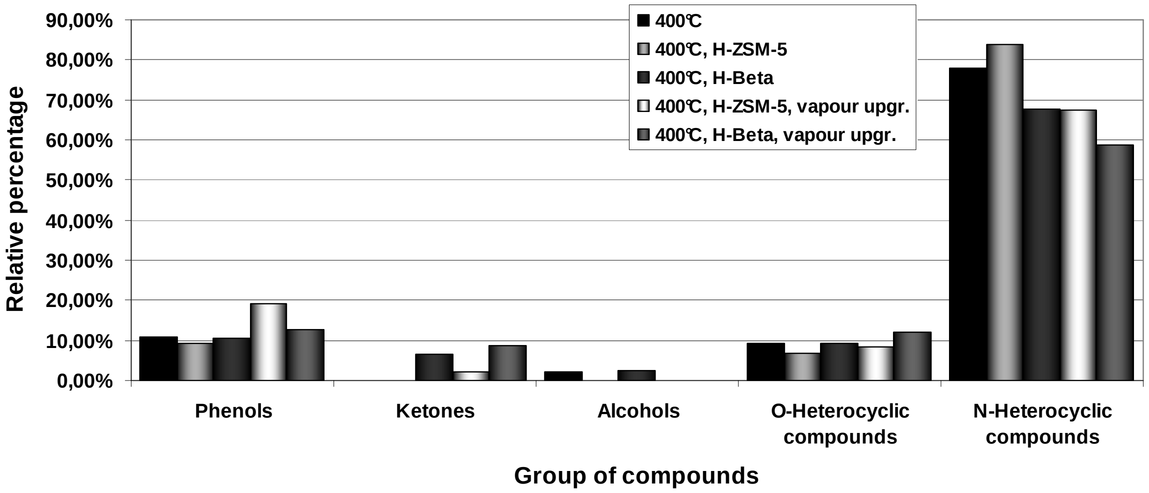


Figure 3-8. Aqueous phase composition of the rapeseed cake conversion liquid products using two reactor configurations

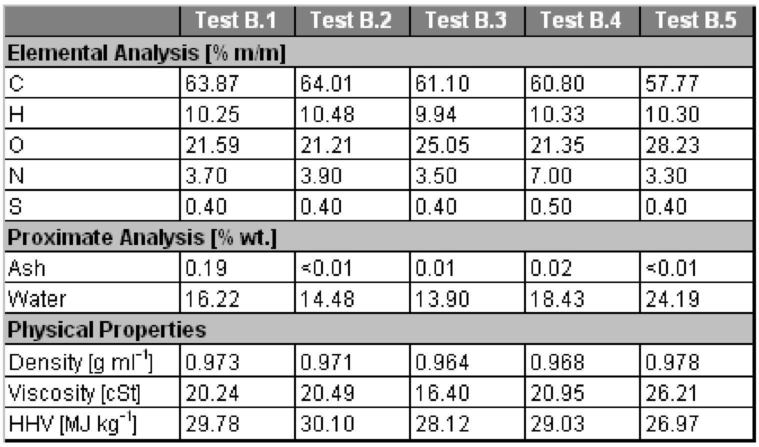
The major group of water-soluble compounds was N-heterocyclic compounds (mainly pyridinol isomers and pyrrole). Their yield was maximized when H-ZSM-5 zeolite was used. The non-catalytic test also produced a high N-heterocyclic compound yield. In the presence of the vapour upgrading section their yields decreased.

The O-heterocyclic compound production (furan derivatives) was significantly low, while the use of the vapour upgrading section increased its yield. The phenol yields were approximately similar in all tests, except when the H-ZSM-5 zeolite was used in the presence of the vapour upgrading section. Ketones were mainly formed on the H-Beta zeolite, while the vapour upgrading section increased their production. The formation of small amounts of alcohols was observed in two tests only.

3.6.2.6 ELEMENTAL COMPOSITION / PHYSICAL PROPERTIES

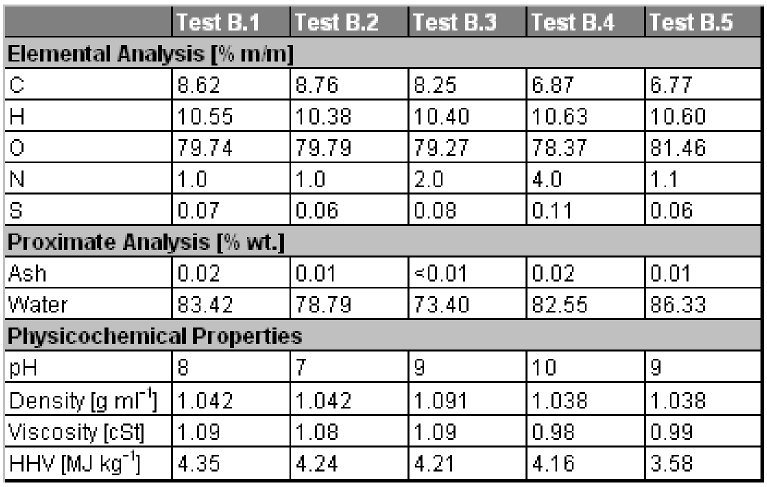
The results of the elemental composition and the physical properties of the produced organic and aqueous phase are depicted in the following Tables:

Table 3-9: Organic phase characteristics of the rapeseed cake conversion tests using two reactor configurations



	Test B.1	Test B.2	Test B.3	Test B.4	Test B.5
Elemental Analysis [% m/m]					
C	63.87	64.01	61.10	60.80	57.77
H	10.25	10.48	9.94	10.33	10.30
O	21.59	21.21	25.05	21.35	28.23
N	3.70	3.90	3.50	7.00	3.30
S	0.40	0.40	0.40	0.50	0.40
Proximate Analysis [% wt.]					
Ash	0.19	<0.01	0.01	0.02	<0.01
Water	16.22	14.48	13.90	18.43	24.19
Physical Properties					
Density [g ml^{-1}]	0.973	0.971	0.964	0.968	0.978
Viscosity [cSt]	20.24	20.49	16.40	20.95	26.21
HHV [MJ kg^{-1}]	29.78	30.10	28.12	29.03	26.97

Table 3-10: Aqueous phase characteristics of the rapeseed cake conversion tests using two reactor configurations



	Test B.1	Test B.2	Test B.3	Test B.4	Test B.5
Elemental Analysis [% m/m]					
C	8.62	8.76	8.25	6.87	6.77
H	10.55	10.38	10.40	10.63	10.60
O	79.74	79.79	79.27	78.37	81.46
N	1.0	1.0	2.0	4.0	1.1
S	0.07	0.06	0.08	0.11	0.06
Proximate Analysis [% wt.]					
Ash	0.02	0.01	<0.01	0.02	0.01
Water	83.42	78.79	73.40	82.55	86.33
Physicochemical Properties					
pH	8	7	9	10	9
Density [g ml^{-1}]	1.042	1.042	1.091	1.038	1.038
Viscosity [cSt]	1.09	1.08	1.09	0.98	0.99
HHV [MJ kg^{-1}]	4.35	4.24	4.21	4.16	3.58

Comparing the elemental analysis data, it is shown that the organic phases produced in the presence of the H-ZSM-5 zeolite showed similar hydrogen and oxygen content with the non-catalytic test. The use of the H-Beta zeolite increased the oxygen content of the organic phase and reduced the carbon content. The vapour upgrading section significantly reduced the carbon contents of the organic phases. Sulfur is one undesirable component of fuels. The sulfur content in the organic phases was low in comparison with fuel oils (sulfur content No. 4 fuel oil and No. 6 fuel oil (according to the classification with the U.S. nomenclature) was reported 1.5-4.0% wt. (Özçimen and Karaosmanoğlu, 2004)).

The pH value of the organic phases was in the basic region and it was considerably higher than the pH value of typical wood pyrolysis oil (2-2.5) (Bridgwater, 1994).

The produced organic phases possessed higher HHV than pyrolysis oils and similar to liquefaction oils (19.3 and 30-35 MJ/kg respectively) (Bridgwater, 1994; Naber et al., 2002). The organic phase HHV increased by the following order: H-ZSM-5 > non-catalytic > H-ZSM-5 (upgr.) > H-Beta > H-Beta (upgr.). The organic phase density was slightly higher than that of diesel (~0.85 g ml^{-1}).

3.6.2.7 CATALYST REGENERATION AND CHARACTERIZATION

The X-Ray diffractograms of the fresh and regenerated zeolites from both the reactor and the upgrading section are depicted in Figure 3-9 for the H-ZSM-5 zeolite and in Figure 3-10 for the H-Beta zeolite.

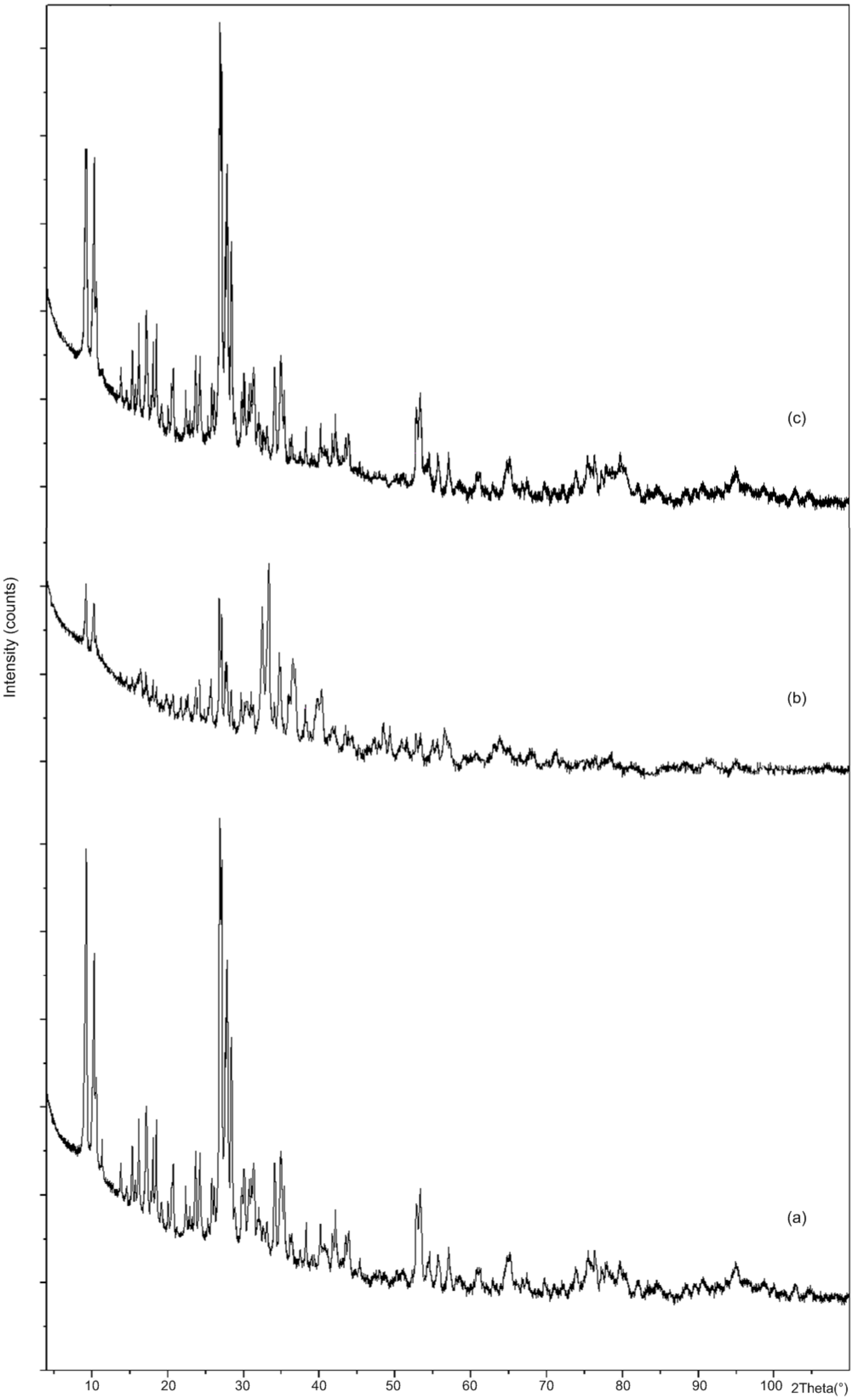


Figure 3-9. XRD patterns of (a) the fresh H-ZSM-5, (b) the regenerated H-ZSM-5 from the reactor and (c) the regenerated H-ZSM-5 from the vapour upgrading section

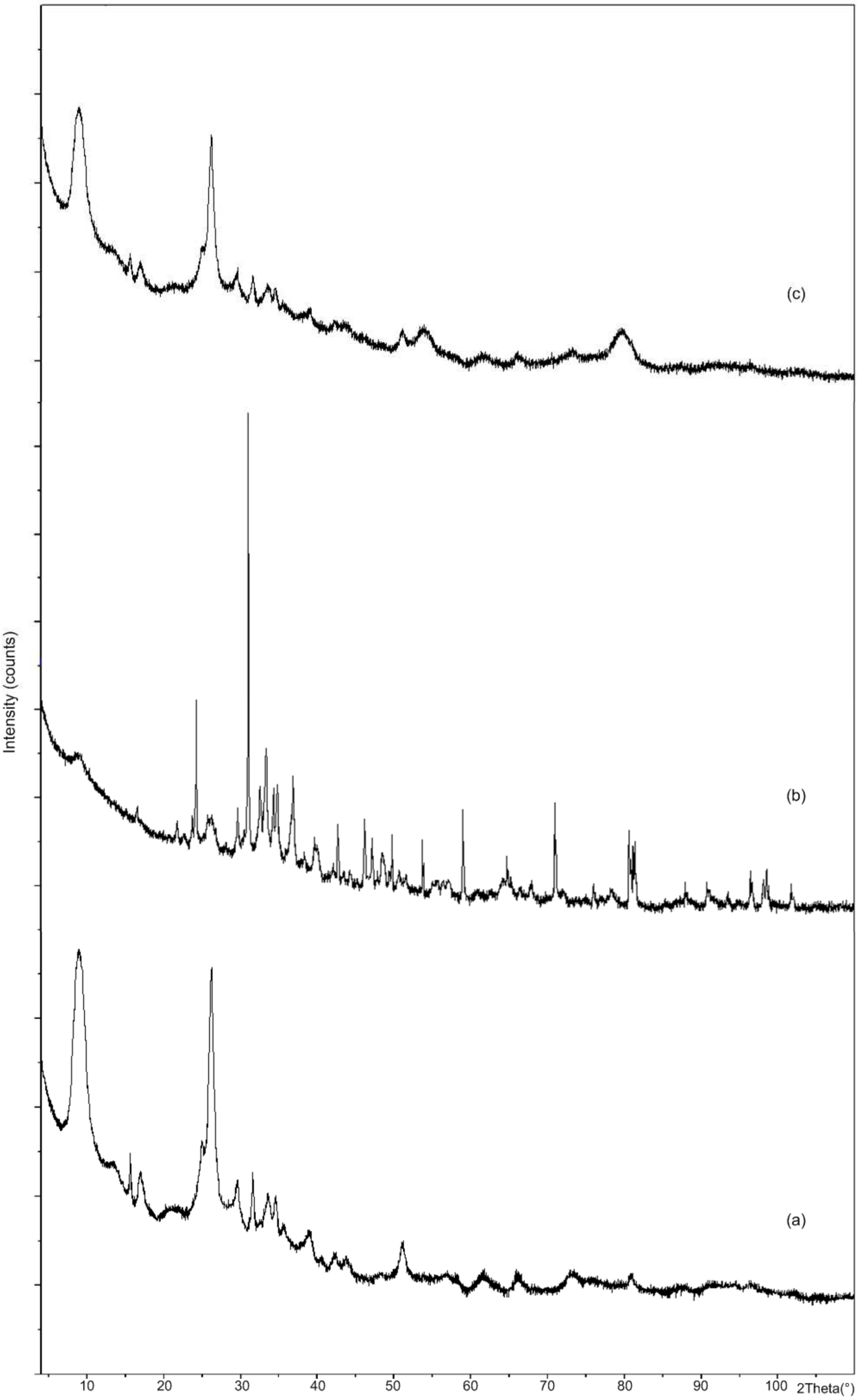


Figure 3-10. XRD patterns of (a) the fresh H-Beta, (b) the regenerated H-Beta from the reactor and (c) the regenerated H-Beta from the vapour upgrading section

In Figure 3-9, the diffractogram comparison of the fresh and regenerated H-ZSM-5 zeolite from the reactor showed obvious similarities. The differences between the two diffractograms indicated the presence of a second phase. The peak heights in the diffractogram of the regenerated sample were lower than for the primary material, which indicated a lower degree of crystallinity. On the contrary, the regenerated H-ZSM-5 zeolite from the vapour upgrading section showed an XRD pattern very similar to the fresh one, which proved its successful regeneration.

In Figure 3-10, the regenerated sample of the H-Beta zeolite from the reactor had a completely different mineralogical composition than that of the fresh material. Mineral phases like quartz could be identified. A broad peak at 9.01° 2θ could point to a very low portion of the H-Beta zeolite. H-Beta zeolite was the main component in the diffractogram of the regenerated material from the vapour upgrading section, although some differences to the primary material were visible, especially at angles greater than 55° 2θ. This indicated a change in the crystalline structure of the material.

3.6.3 MEAT MEAL C1 AND ALGAE CONVERSION

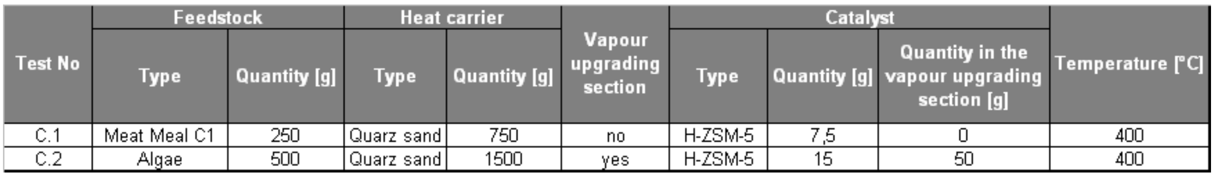
3.6.3.1 SCIENTIFIC BACKGROUND

Apart from edible feedstocks that have been used for biofuel production (e.g. oils/fats, starch, sugar), focus has been given in non-edible biogenic sources. Presently, meat meal C1 is mainly incinerated, because it is considered to be a high health risk material. If meat meal C1 is utilized in a different way, products with higher added-value may yield. Algae has been gathering increased attention as a feedstock for biofuel production, due to the fact that its chemical composition can be regulated according to the used cultivation conditions as well as its increased productivity in non-arable land. Both biogenic materials have been selected as feedstocks for the KNV process in order to explore their conversion into biofuels.

3.6.3.2 PERFORMED TESTS

The following tests were performed (set of tests: C):

Table 3-11: Performed tests overview of the separate meat meal C1 and algae conversion (with different reactor configurations)



Test No	Feedstock		Heat carrier		Vapour upgrading section	Catalyst			Temperature [°C]
	Type	Quantity [g]	Type	Quantity [g]		Type	Quantity [g]	Quantity in the vapour upgrading section [g]	
C.1	Meat Meal C1	250	Quarz sand	750	no	H-ZSM-5	7,5	0	400
C.2	Algae	500	Quarz sand	1500	yes	H-ZSM-5	15	50	400

Test C.1 was performed in the absence of the vapour upgrading section, while test C.2 was performed in the presence of the vapour upgrading section. For test C.1, 250 g of the starting feedstock was used instead of 500 g, which was the standard quantity of solid feedstock for the previous experiments. The reason for this was the nature of meat meal C1, which created thin powder during the experiments. The lower the quantity of starting meat meal C1, the lower the quantity of the produced thin powder. Consequently, blockages in the piping network of the system could be avoided.

3.6.3.3 PHASE COMPOSITION OF THE REACTION MIXTURE

In each experiment the mixture of the organic liquid phase, the aqueous liquid phase, the solid residue and the gases were obtained. The liquid products consisted of two well separated phases: an organic and an aqueous phase. The relative contents of these phases depended on the feedstock and reactor configuration (Figure 3-11).

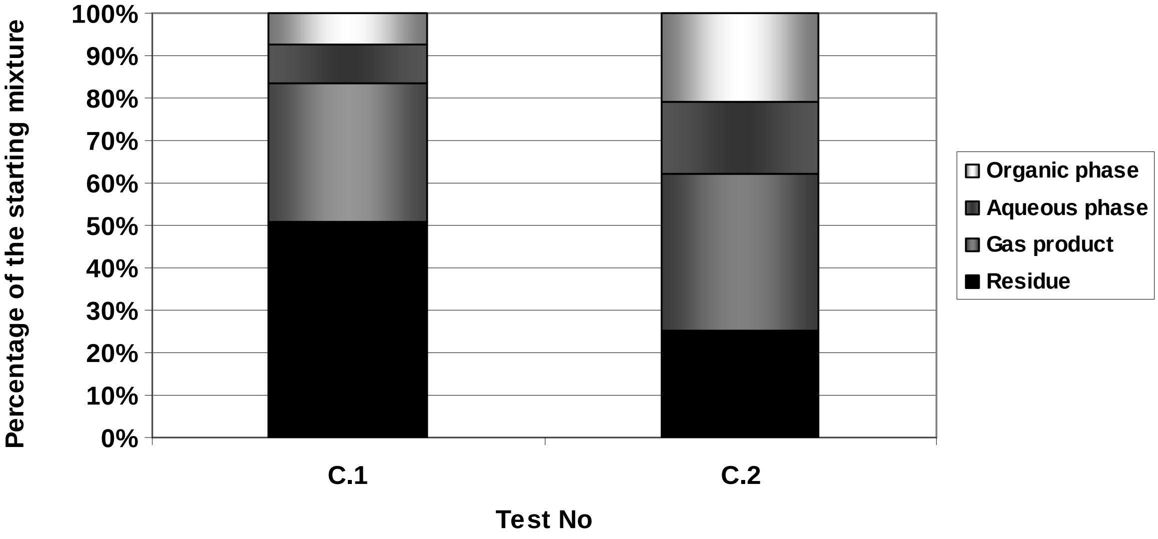


Figure 3-11. Product yields (wt. % on biogenic mixture) of the performed separate meat meal C1 and algae conversion tests

The meat meal C1 conversion demonstrated a significantly high residue production (~51%), while the gas production prevailed over the liquid production. The ratio of organic to liquid product was approximately 1:1.

Algae in the presence of the vapour upgrading section and H-ZSM-5 zeolite gave a higher liquid production and a lower residue production compared with the rapeseed cake test, using the same parameters. The organic phase yield was also maximized when the algae was used.

CO_2 and light hydrocarbons (C2-C6) were present in the gas phases.

3.6.3.4 CHEMICAL COMPOSITION OF THE ORGANIC PHASE

The chemical composition of the organic phases, gained at different tests, is depicted in the following Figure:

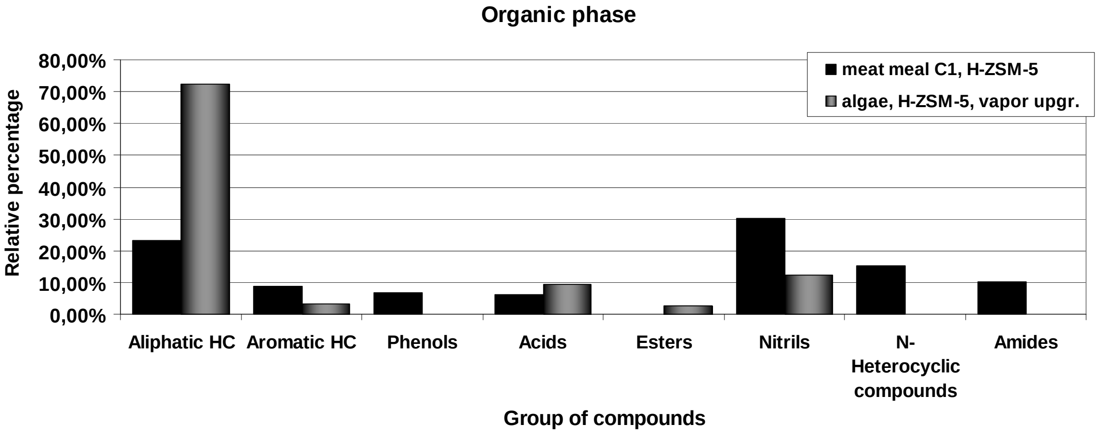


Figure 3-12. Organic phase composition of the separate meat meal C1 and algae conversion liquid products

Meat meal C1 conversion, with H-ZSM-5 zeolite in the absence of a vapour upgrading section, produced a higher yield of hydrocarbons (aliphatic and aromatic: ~32%) compared with the rapeseed cake conversion (~23%). The amide and nitril production was increased when meat meal C1 was used (~40%) compared with that of rapeseed cake (~30%) at the expense of acids (~6% and ~20% respectively). The N-heterocyclic compound yield of meat meal C1 (~15%) was higher than that of rapeseed cake (~5%), while a small quantitiy of phenols was present in the organic phase.

The catalytic conversion of algae in the presence of H-ZSM-5 zeolite and the vapour upgrading section resulted in the production of an organic phase with a higher content of hydrocarbons (~75%, aliphatic and aromatic hydrocarbons) compared with the rapeseed cake test. Limited production of acids and nitrils was demonstrated, while no phenols, N-heterocyclic compounds and amides were present.

3.6.3.5 CHEMICAL COMPOSITION OF THE AQUEOUS PHASE

The aqueous phase contained phenols, ketones, O-heterocyclic compounds and N-heterocyclic compounds:

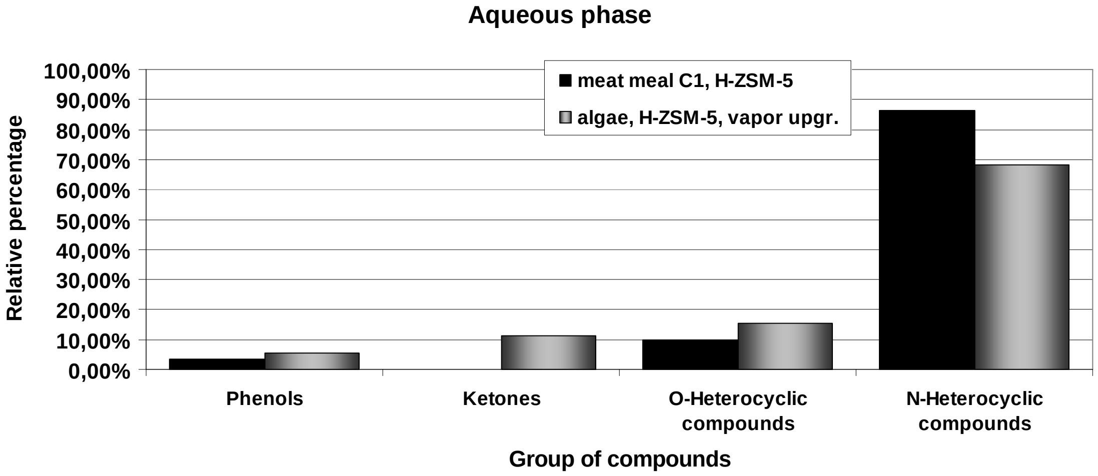


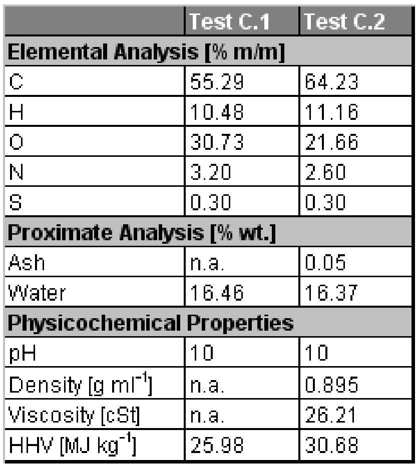
Figure 3-13. Aqueous phase composition of the separate meat meal C1 and algae conversion liquid products

Both feedstocks favored the significant formation of N-heterocyclic compounds. Algae and rapeseed cake in the presence of H-ZSM-5 and the vapour upgrading section, gave equal contents of N-heterocyclic compound. Algae demonstrated a higher production of ketons and O-heterocyclic compounds than rapeseed cake. In the case of meat meal C1, phenols were distributed between organic and aqueous phases.

3.6.3.6 ELEMENTAL COMPOSITION / PHYSICAL PROPERTIES

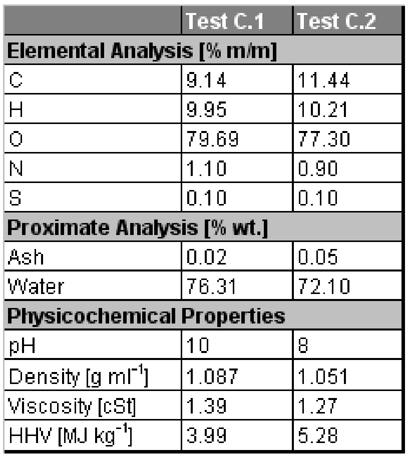
The results of the elemental composition and the physical properties of the produced organic and aqueous phase are depicted in the following Tables:

Table 3-12: Organic phase characteristics of the separate meat meal C1 and algae conversion tests



	Test C.1	Test C.2
Elemental Analysis [% m/m]		
C	55.29	64.23
H	10.48	11.16
O	30.73	21.66
N	3.20	2.60
S	0.30	0.30
Proximate Analysis [% wt.]		
Ash	n.a.	0.05
Water	16.46	16.37
Physicochemical Properties		
pH	10	10
Density [g ml^{-1}]	n.a.	0.895
Viscosity [cSt]	n.a.	26.21
HHV [MJ kg^{-1}]	25.98	30.68

Table 3-13: Aqueous phase characteristics of the separate meat meal C1 and algae conversion tests



	Test C.1	Test C.2
Elemental Analysis [% m/m]		
C	9.14	11.44
H	9.95	10.21
O	79.69	77.30
N	1.10	0.90
S	0.10	0.10
Proximate Analysis [% wt.]		
Ash	0.02	0.05
Water	76.31	72.10
Physicochemical Properties		
pH	10	8
Density [g ml^{-1}]	1.087	1.051
Viscosity [cSt]	1.39	1.27
HHV [MJ kg^{-1}]	3.99	5.28

Comparing the elemental analysis data, it is shown that the organic phase produced during the algae conversion had a lower oxygen content as well as a higher carbon and hydrogen content compared with that of meat meal C1. The organic phase of meat meal C1 had a higher oxygen and a lower carbon content than that of rapeseed cake.

The sulfur content in the organic phases was low in comparison with No. 4 fuel oil and No. 6 fuel oil (according to the classification with the U.S. nomenclature) (1.5-4.0% wt.) (Özçimen and Karaosmanoğlu, 2004).

The pH value of the organic phases was in the basic region and it was considerably higher than the pH value of typical wood pyrolysis oil (2–2.5) (Bridgwater, 1994).

The produced organic phases showed lower oxygen content than pyrolysis oils (30-37% wt.) (Naber et al., 2002; Bridgwater 1994). The density of the algal organic phase was slightly higher than that of diesel (~0.85 g ml^{-1}).

The produced organic phases possessed higher HHV than pyrolysis oils (19.3 MJ/kg). The organic phase of the algae conversion possessed similar HHV to liquefaction oils (30-35 MJ/kg) (Bridgwater, 1994). Algae produced the organic product with the highest HHV compared with that of rapeseed cake and meat meal C1 conversion tests.

3.7 DISCUSSION OF RESULTS

3.7.1 CO-CONVERSION OF RAPESEED CAKE AND SAFFLOWER OIL

3.7.1.1 PHASE COMPOSITION OF THE REACTION MIXTURE

At 400 °C, the addition of zeolite catalyst to the feedstock significantly affected the phase composition of the product mixture. This is expected due to the catalyzing effect of zeolite in cracking and other acid-catalyzed reactions, leading to intensive formation of compounds with lower molecular weight.

At both process temperatures, the structural characteristics of the H-Beta zeolite were responsible for the lower production of residues and the higher production of liquids. The pore size of this zeolite is large enough (7.7 Å) to provide access of bulky molecules to its strong acidic sites and to perform their cracking to smaller molecules. The H-ZSM-5 zeolite has stronger acidic sites than H-Beta (Hegde et al., 1989), but smaller pores (5.6 Å). Thus, the cracking ability of this catalyst is limited by its shape-selectivity that reduced the liquid product and gas yield. In contrast, the activity in polymerization (leading to coke formation) does not require very strong catalyst acidity and remains high. As a result, the solid residue yield increased.

The effect of shape-selectivity is still enhanced with the hydrogen exchange in ZSM-5 zeolite with bigger Fe^{3+} cations. In addition, the Fe exchanged form of ZSM-5 zeolite has a lower total acidity at the absence of very strong acidic sites compared with H-ZSM-5 zeolite (Das et al., 1995). In the presence of Fe-ZSM-5 zeolite, the rate of reactions proceeding on strong acidic sites was still lower than on H-ZSM-5 zeolite, while polymerization and coking became the predominant processes.

The same relative behavior of the catalysts was observed at both process temperatures. However, the liquid product yield at 350 °C was significantly lower, while the main conversion product was solid residue. As it is known, the acid-catalyzed polymerization reactions (responsible for coking) easily proceed at lower temperature, while cracking requires much harder conditions.

At 350 °C, the significant reduction of the liquid product yield and the residue increase could be explained by the reduced zeolite catalytic activity at lower temperature. But more probably, safflower oil was not completely hydrolyzed to fatty acids at this temperature and the liquid oil intensively polymerized on the acidic sites of zeolites.

At 350 °C, the higher aqueous phase and the lower organic phase yield on the Fe-ZSM-5 zeolite could be explained by the enhanced activity of Fe-ZSM-5 in oxidative dehydrogenation that produces more water and water-soluble heterocyclic and other highly oxygenated compounds.

3.7.1.2 CHEMICAL COMPOSITION OF THE ORGANIC PHASE

The biofuel is mainly composed of water-insoluble substances that form the organic phase of liquid products. The quality of a liquid biofuel can be estimated by the presence of compounds that are also present in conventional petroleum fuels. Therefore, the presence of aliphatic and aromatic hydrocarbons enhances the quality of a liquid biofuel. The presence of phenolic compounds can also be beneficial, since in conventional fuels limited quantities of oxygenated compounds, such as alcohols and ethers, are added to increase the anti-knocking behavior (Stournas et al., 2000). The increased presence of carbonyl compounds (acids, esters, ketones, aldehydes) in a liquid biofuel reduces its quality. The low pH values makes difficult its application in engines due to corrosion, while the increased oxygen content reduces its heating value and alters its physical properties, e.g. volatility. Finally, the increased concentration of nitrogen containing compounds is lowering the biofuel quality, since NO_x emissions are released during the fuel combustion. Still, nitrogen containing compounds, such as alkylesters of nitric acid are used as additives in order to increase the cetane number of diesel (Stournas et al., 2000).

The catalytic and non-catalytic conversion of fatty oil and biomass involves a large variety of individual reactions. The most important of them are cracking/alkylation, hydrogenization/dehydrogenization and hydration/dehydration. Other types of reactions (heterocyclization, esterification, etc.) can also occur. These reaction rates are significantly affected by the presence of a catalyst and its characteristics, such as acidity, pore size and chemical composition. Thus, the catalysts with stronger acidic sites increase the rate of reactions proceeding with an ionic mechanism (cracking, alkylation); small pore size catalysts are more selective in the smaller molecule formation, while the metal-containing zeolites catalyze reactions with a radical mechanism (hydrogenization and dehydrogenization).

At 400 ℃, H-ZSM-5 and H-Beta zeolites produced more light hydrocarbons (alkanes and olefins C7-C14) in comparison with Fe-ZSM-5 zeolite. The products of cracking of heavier hydrocarbons (C15-C17) were light hydrocarbons. Heavier hydrocarbon yields respectively reduced on the H-forms of zeolites. The Fe-ZSM-5 zeolite had a significantly lower cracking ability that resulted in higher contents of heavier hydrocarbons in the product mixture. The absence of light olefins on this catalyst can be explained by its hydrogenating ability due to the presence of transition metal cations. Another important characteristic of the Fe-ZSM-5 zeolite is its activity in aliphatic hydrocarbon aromatization. The yield of aromatic hydrocarbons on this catalyst is twice higher than on H-forms of zeolites. In particular, tridecylbenzene was formed only on this catalyst.

Another large group of the organic phase components is fatty acids. They were obtained at the high-temperature hydrolysis of safflower oil. As these compounds are primary products of the process, the acid content in the reaction mixture depends on their further conversion to other compounds. Nitriles are produced from carboxylic acids in the presence of ammonia and a dehydration catalyst (Denton and Bishop, 1953). The highest yield of fatty acids (and respectively, the lowest yield of hydrocarbons and nitriles) was found on the H-ZSM-5 zeolite. Based on these data it can be concluded that the fatty acid conversion requires the presence of metal in the catalyst, while acidic site strength is not very important. In addition, the zeolite pore size plays a significant role in its ability to catalyze the acid conversion due to steric hindrances.

At 400 ℃, the cracking processes prevailed over alkylation for all zeolite catalysts: the alkylphenols amount was very low, especially on strongly acidic H-forms of zeolites. In particular, dodecylphenol formed during the non-catalytic conversion was not detected in the reaction mixture after all the catalytic experiments. As it was expected, the fatty oil conversion into hydrocarbons was the lowest at the non-catalytic test due to the absence of acidic sites necessary for cracking. However, at these conditions fatty acids were still able to transform into nitriles. Also, the non-catalytic test favored the fatty acid esterification.

At 350 °C, the strong acidity of the H-ZSM-5 zeolite became a more important factor of its activity than the steric limitations caused by its smaller pore size. At 350 °C, the less acidic H-Beta and Fe-ZSM-5 zeolites appeared less active.

Comparing the zeolite catalytic activity, it should be taken into account that all liquid product yields decreased considerably at this temperature. Thus, a relative degree of catalyst deactivation can be estimated.

The Fe-ZSM-5 zeolite showed increased dehydrogenation and aromatization ability, leading to higher aromatic hydrocarbon and olefin yield compared with the H-forms of zeolites. In contrast to H-forms of zeolites, its alkylation ability predominates over cracking (Choudhary et al., 1999) that resulted in the formation of substituted benzenes. The limited diffusion of long-chain olefins to the active sites, due to the shape-selectivity effect, led to the formation only of alkylbenzenes with shorter alkyl groups (up to C9) on this catalyst.

Due to the insufficient cracking ability of Fe-ZSM-5 zeolite, the gained liquid phase contained a significant amount of unreacted linoleic acid. In the case of the more acidic H-ZSM-5 zeolite, linoleic acid was completely converted to other compounds.

The very low amount of nitriles found in the product mixture may be caused by the insufficient formation of ammonia at the low-temperature biomass cracking. The relative nitrile yields correlate with the catalysts cracking ability.

3.7.1.3 CHEMICAL COMPOSITION OF THE AQUEOUS PHASE

The biomass conversion processes offer the possibility for the production not only of biofuel but also of biochemicals. In particular, the aqueous phase could be utilized for the extraction of chemical compounds with high added value. For example, nitrogen containing compounds can be used in a variety of applications in pharmaceutical, plastic and food industry (Higashio and Shoji, 2004). Additionally, oxygen containing compounds can be used for the production of bio-polymers and other chemicals (Bridgwater, 1994).

The highest yields of short-chain acids (mainly acetic and propanoic) were observed on H-ZSM-5 and H-Beta zeolites. As they are primary products of fatty acid and O-heterocyclic compound cracking, it was expected that the catalysts with stronger acidic sites would favor their formation. In contrast, the short-chain acid yield at the non-catalytic test was minimized.

Phenolic compounds are the typical lignin cracking products. Their yields were higher at use of highly acidic H-ZSM-5 and H-Beta catalysts. The Fe-ZSM-5 zeolite did not show sufficient cracking ability and, therefore, phenol yield was twice lower than that on H-forms of zeolites. It should be noted that the Fe-ZSM-5 zeolite did not produce any diols.

O-heterocyclic compounds were formed during the carbohydrate dehydration. Carbohydrates are decomposition products of polysaccharides. The O-heterocyclic compound yields slightly depended on the presence of a catalyst, since the cellulose and hemicellulose dehydration easily proceeded even at the absence of a catalyst. The lower O-heterocyclic compound yield on the Fe-ZSM-5 zeolite can be explained by their catalytic conversion to other compounds (such as N-heterocyclic compounds or ketones) on metal-containing zeolite (for example via furan–pyrrole ring-exchange, Hatada et al., 1974). As a result, the yields of products that belong to these two groups on the Fe-ZSM-5 zeolite are the highest among all catalysts.

The N-heterocyclic compound formation can occur due to the reaction of ammonia with O-heterocyclic compounds, as well as at the direct decomposition of biomass components. The H-ZSM-5 zeolite led to their lower yield, probably due to its higher cracking ability that favors further conversion of N-heterocyclic compounds to smaller molecules.

As shown in Figure 3-5, the higher acid formation on the H-Beta zeolite clearly proves that the effect of shape-selectivity at lower temperature plays a critical role in the conversion of large molecules of fatty acids and O-heterocyclic compounds. The low Fe-ZSM-5 zeolite acidity and its small pore size were responsible for the reduced acid yield when this catalyst was used.

The profile of the catalyst activity in the formation of phenols, ketones, alcohols and N-heterocyclic compounds at 350 ℃ was the same as at 400 ℃.

3.7.1.4 ELEMENTAL COMPOSITION / PHYSICAL PROPERTIES

The oxygen content is an important characteristic of the biofuel. As deoxygenation occurs during the fatty oil and biomass cracking, it was expected that catalysts with high acidity would produce an organic phase with lower oxygen content, like H-Beta zeolite in this case. The lower deoxygenation ability of the H-ZSM-5 zeolite was attributed to its smaller pore size that restricted the access of large substrate molecules to its active sites. The weaker acidity of the Fe-ZSM-5 zeolite further reduced the deoxygenating ability of this catalyst. The produced organic phases showed a lower oxygen content than pyrolysis and liquefaction oils (30-37% wt. and 10-18% wt. respectively) (Bridgwater 1994; Naber et al., 2002).

At 400 ℃, the water contents correlate with the deoxygenation degree of the organic phase: the mixture gained on the H-Beta zeolite has the lowest oxygen and, respectively, water content. In contrast, the Fe-ZSM-5 zeolite resulted in the formation of more oxygenated organic phase, containing a higher water amount. Evidently, highly oxygenated compounds in the organic phase are polar and absorb the water, forming complexes with water molecules.

The pH values depend on the carboxylic acid and phenols concentration in the mixture. Since the mixture obtained at 350 ℃ contained less fatty acids, its pH value was still higher than that the organic phase obtained at 400 ℃.

The quality of a fuel is characterized by its HHV. This depends on the deoxygenation degree: the high oxygen content of a fuel reduces its HHV. Thus, the organic phase HHV obtained at 400 ℃ follows the same order as their oxygen content: Fe-ZSM-5 < non-catalytic < H-ZSM-5 < H-Beta. The same correlation between HHV and oxygen content was observed for the organic phases obtained at 350 ℃.

Not only the presence of oxygen but also the ash content affects the HHV of residues. While ash amount in the liquid phase is insignificant, for the residues it plays a notable role, reducing their HHV. At 400 ℃, the HHV decreased in the following order: non-catalytic > Fe-ZSM-5 > H-ZSM-5 ≃ H-Beta. For the first three experiments it correlated with the oxygen content, but in the case of the H-Beta zeolite, the HHV was significantly lower than expected due to the high ash content.

3.7.2 RAPESEED CAKE CONVERSION WITH TWO REACTOR CONFIGURATIONS

3.7.2.1 PHASE COMPOSITION OF THE REACTION MIXTURE

The addition of a zeolite catalyst to the feedstock considerably affected the phase composition of the product mixture. Both zeolites catalyzed the lignin and polysaccharide cracking of the biomass. Another reaction catalyzed by zeolites was the polymerization of formed unsaturated compounds, which could result in the solid residue production. The relative rate of these reactions depended on the zeolite structural and acidic properties. Thus, the strongly acidic H-ZSM-5 zeolite possessed a higher activity in cracking, which led to the intensive formation of compounds with lower molecular weight. As a result, the gas product yield increased, while the amount of formed residue was lower in comparison with that of the H-Beta catalyst. In contrast to cracking, polymerization reactions (leading to the coke formation) do not require very strong acidic sites on the catalyst. Therefore, the H-Beta zeolite favored coking. Both zeolites did not show a notable difference in the liquid product yield.

The recycled condensed vapours got again in contact with the catalyst inside the biogenic mixture. In the case when the vapour upgrading section was added into the system, the recycled condensed vapours got in contact with the catalyst in the vapour upgrading section.

In the presence of the vapour upgrading section, the biomass conversion to non-condensable gases should have increased, while the liquid product and coke formation should have decreased. The higher activity of H-Beta zeolite in the vapour upgrading section was attributed to the creation of clefts or mesopores in the zeolite crystallites by hydrothermal treatment. As a result, the diffusion pathways, leading to the active sites inside the pores, were shortened and the site availability was considerably increased (Van Bokhoven et al., 2002).

On the contrary, the hydrothermal treatment of the H-ZSM-5 zeolite resulted in the dealumination of the material, which led to the micropore blockage of the material, making active sites inaccessible for reactants (Fan et al., 2006). This was evident from the reduced liquid and gas yields, while the coke formation increased. It has been reported that hydrothermal dealumination followed by subsequent citric acid treatment can have as an effect the realumination of the zeolite. In our case, the realumination of the H-ZSM-5 zeolite could have been possible in the presence of carboxylic acids. Still, based on the obtained data it seemed that it had a minor effect in the presented results, probably due to the weaker acidity of fatty acids in comparison with citric acid.

The organic phase production was increased by the following order: HZSM-5 (upgr.) > H-Beta > H-ZSM-5 > non catalytic > H-Beta (upgr.). The lowest water-insoluble compound yield was observed on the H-Beta zeolite with the vapour upgrading section. This might be caused by the deep catalytic cracking of biomass into gas and liquid products with low molecular weight. In the case of the H-ZSM-5 zeolite with the vapour upgrading section, the lower activity of the vapour-treated catalyst slowed the biomass deep cracking, increasing the organic product yield.

3.7.2.2 CHEMICAL COMPOSITION OF THE ORGANIC PHASE

Biofuel is mainly composed of water-insoluble substances that form the organic phase of liquid products. The main groups of compounds produced by the rapeseed cake conversion were fatty acids and their derivatives: esters, amides and nitriles. The fatty acids were formed by the high temperature hydrolysis of fatty oils. As these compounds (mainly oleic acid) were the primary products of the process, the acid contents in reaction mixtures depended on their further conversion to other compounds. The HZSM-5 zeolite showed higher activity in the fatty acid conversion, due to the presence of strong acidic sites that favored cracking to hydrocarbons, their esterification and transformation to nitriles through the intermediate amide formation. The amides were formed by the reaction of acids with amines or ammonia. The further conversion to nitriles requires the presence of a dehydration catalyst of acidic nature (Denton and Bishop, 1953). The conversion of fatty acids to amides and nitriles is a reversible process. As we can see from experimental data, the presence of a catalyst shifts the equilibrium to acids while non-catalytic conversion results in higher contents of nitriles.

Yields of nitriles also depend on cracking ability of the catalyst. The HZSM-5 zeolite provided a higher fatty acid cracking degree to hydrocarbons that reduced the nitrile yields in comparison with the H-Beta zeolite. In contrast, the less acidic H-Beta zeolite did not favor the fatty acid cracking, resulting in its further conversion into nitriles. Amides are the intermediate compounds in the nitrile formation, thus, their yields depended on the relative rate of both acid amidation and amide dehydration. The insufficient Brønsted acidity of the hydrothermally treated catalysts in the vapour upgrading section resulted in an increased amount of unreacted acids and a reduced production of esters and nitriles.

Hydrocarbons are valuable components of bio-oils and can improve their fuel properties. Hydrocarbon yields depended on the zeolite acidity and correlated with the fatty acid conversion. The most acidic H-ZSM-5 zeolite provided the highest aliphatic hydrocarbon yields (C8-C17). This catalyst also enhanced the aromatic hydrocarbon production due to its aromatization ability, as it’s known from other references (Williams and Nugranad, 2000; Chew and Bhatia, 2008). It is evident that the presence of the upgrading section reduced the aliphatic hydrocarbon yields.

Two other groups of compounds were present in both organic and aqueous phases. Phenols were products of lignin decomposition, and N-heterocyclic compounds formed from amines and ammonia that was released during the decomposition of proteins. Pyrrole was primarily formed and then it partially converted to indole, which is a product of cycloaddition. These two compounds readily polymerized in the presence of acids. Thus, their relative contents in the reaction mixture depended on the catalyst polymerizing ability.

The presence of phenolic compounds can also be beneficial, since limited presence of oxygenated compounds can improve the anti-knocking behaviour of conventional fuels (Stournas et al., 2000). The phenol yield was maximized when the HZSM-5 zeolite was used in the presence of the vapour upgrading section, since steric hindrances on this zeolite prevented their further decomposition.

Carbonyl and N-containing compounds reduce the quality of biofuels. Thus, the low pH values of acid-rich oils results in metal corrosion; increased oxygen content reduces the biofuel HHV and alters its physical properties, e.g. volatility; and N-containing compounds are responsible for NOx emissions during fuel combustion. They must be eliminated from bio-oils at its further conversion to biofuel. However, nitrogen containing compounds, such as alkylesters of nitric acid are used as additives in order to increase the diesel cetane number (Stournas et al., 2000).

3.7.2.3 CHEMICAL COMPOSITION OF THE AQUEOUS PHASE

In spite of the low rapeseed cake nitrogen content, N-containing compounds were the major components of the aqueous phase due to their solubility in water. The main nitrogen source was rapeseed cake proteins that thermally decomposed during the process. The aminoacid content in dry rapeseed cake (mainly arginine, lysine, methionine, cysteine, threonine and tryptiphan) usually varies between the range of 7-9% wt. (Leming and Lember, 2005). As it has been reported, the main routes of aminoacids decomposition are decarboxylation and deamination (Klingler et al., 2007; Peterson et al., 2008). In the performed tests, the produced ammonia and lower amines further reacted with other compounds of the reaction mixture. The highest N-heterocyclic compound yields were reached when the H-ZSM-5 zeolite was used, due to the presence of strong acidic sites involved in the reactions of natural substance decomposition. In formation of N-heterocyclic compounds at non-catalytic test carboxylic acids of the reaction mixture may play the role of a catalyst.

O-heterocyclic compounds (mainly furan-2-methanol) were formed from carbohydrates, which are products of the polysaccharide decomposition (Karagöz et al., 2005; Román-Leshkov et al., 2007). Their yields slightly depended on the presence of a catalyst, since cellulose and hemicellulose dehydration easily proceeded even at non-catalytic conditions. The vapour upgrading section increased the O-heterocyclic compound yields, probably due to slowing their further destruction into low molecular weight products.

Phenols and their derivatives (including methoxyaromatic compounds) are products of lignin decomposition (Karagöz et al., 2005). Compounds of this group are distributed between organic and aqueous phases. Their total yields were approximately similar for all tests, except from the vapour upgraded H-ZSM-5 zeolite. The higher phenolic compound yield on this catalyst could be explained by the additional formation of phenols from O-heterocyclic compounds. Thus, 4-methyl-2,6-di-tert-butylphenol was formed from both lignin and cellulose (Karagöz et al., 2005).

Alcohols and ketones are other products of the carbohydrate degradation. They formed mainly on the H-Beta zeolite, because its wide pores provided higher accessibility of the reacting molecules to the active sites.

3.7.2.4 ELEMENTAL COMPOSITION / PHYSICAL PROPERTIES

The pH value of both the organic and aqueous phase was in the basic region (≥7). The highest pH was observed in the liquid products gained after the biomass conversion with H-ZSM-5 zeolite in the presence of the vapour upgrading section. This correlated with the high nitrogen content of both organic and aqueous phases. This effect could be attributed to the presence of dissolved ammonia and/or lower amines formed during the protein decomposition. Their further conversion to less basic compounds was restricted by the blocking of zeolite pores by the extraframework aluminum.

When H-ZSM-5 zeolite was used, the oxygen content of the organic phases was similar to that of the non-catalytic test. Additionally, when H-Beta zeolite was used, the oxygen content of the organic phases was higher than that of the non-catalytic test. In contrast, the total oxygen content of the liquid products of all catalytic tests, except from Test 5, was lower than that of the non-catalytic test (63.24%, 61.90%, 62.64%, 56.02%, and 65.60% respectively). The high activity of zeolite H-Beta, in the presence of the vapour upgrading section, had as a result the maximum total water production compared with all other tests. Therefore, the total oxygen content in the liquid product was higher than in the case of the non-catalytic run.

The HHV of organic phases correlates with their elemental composition. The H-ZSM-5 zeolite provided the highest degree of deoxygenation. Thus, the mixture obtained on this catalyst had the highest (C+H)/O ratio, providing the highest HHV. The high oxygen content of the organic phase, gained with the H-Beta zeolite and the vapour upgrading section, resulted in a reduced HHV.

3.7.2.5 CATALYST REGENERATION AND CHARACTERIZATION

The regeneration by thermal treatment has as a result changes in the acidic and structural properties of the zeolite catalysts. The number of Lewis acid sites increase at the expense of

Brønsted acidity. The thermal treatment affects the structural characteristics of the materials, causing their partial amorphization or formation of new crystalline phases.

The spent catalysts from the reactor were contaminated by the highly viscous residue, product of the conversion process, making their efficient regeneration more difficult. During the thermal treatment, the high coke concentration on the catalytic material could have led to local overheating and disruption of the crystalline structure.

As XRD results showed, the regeneration of the spent catalyst from the vapour upgrading section was more successful than from the reactor. Thus, the H-ZSM-5 zeolite from the vapour upgrading section showed improved regeneration ability. As it was already mentioned, the steam treatment of zeolites results in their partial dealumination and, respectively, increases their Si/Al ratio. The crystalline structures of highly siliceous zeolites are more stable against acids and thermal treatment. As it is shown from X-Ray diffractograms of the fresh and regenerated H-ZSM-5 zeolite, the crystallinity loss of this catalyst was insignificant. However, the activity of stabilized zeolite was lower due to the reduced framework aluminum content and the increased steric hindrances.

In the case of the H-Beta zeolite, its stability was very low even in the vapour upgrading section. In contrast to the H-ZSM-5 zeolite, the reduced peaks in X-Ray diffractogram of H-Beta showed its notable amorphization. As to the H-Beta catalyst from the reactor, its crystalline structure was completely destroyed.

3.7.3 MEAT MEAL C1 AND ALGAE CONVERSION

3.7.3.1 PHASE COMPOSITION OF THE REACTION MIXTURE

Meat meal contains an increased amount of inorganic components compared with other feedstocks. Biomass thermochemical conversion is expected to be catalyzed by small ash amounts. Higher ash amounts are assumed to have a negative influence on the biomass conversion, therefore this could explain the low liquid product yield during the meat meal conversion under the selected operational conditions.

The significantly low residue production during the algae conversion could be attributed to the reduced lignin content of the raw material. The significantly high liquid production could be explained by the increased oil content of the algae. The oil content of the feedstock also resulted in a maximized organic phase yield compared with the rapeseed cake test.

3.7.3.2 CHEMICAL COMPOSITION OF THE ORGANIC PHASE

The hydrocarbon production (aliphatic and aromatic) was higher for the meat meal C1 than for the rapeseed cake, due to the higher fat content of meat meal C1 compared with the oil content of rapeseed cake. The acids in the meat meal organic phase were further converted into amides and nitrils. This could be attributed to the increased protein content of the meat meal C1 compared with that of rapeseed cake, which could promote the ammonia addition. The increased protein content of the meat meal could explain the increased N-heterocyclic compound yield compared with that of rapeseed cake.

The significant oil content of the algae resulted in an important production of aliphatic and aromatic hydrocarbons, which are important components for biofuel production. The presence of H-ZSM-5 zeolite in the reaction mixture and in the vapour upgrading section promoted decarboxylation and cracking reactions and resulted in a wide carbon chain length (C8-C17). The nitril production prevailed over the amide production, since the H-ZSM-5 zeolite resulted in more intensive acid dehydration. The reduced lignin content of algae resulted in a reduced production of phenols in the organic and aqueous phase.

3.7.3.3 CHEMICAL COMPOSITION OF THE AQUEOUS PHASE

N-heterocyclic compounds are the major components of aqueous phase for both feedstocks, due to their solubility in water. The main source of nitrogen is the feedstock proteins that thermally decomposed at the process conditions. The higher yield of N-heterocyclic compounds was reached when meat meal C1 was converted, due to its increased protein content compared with that of rapeseed cake.

Phenols could be products of the lignin or protein decomposition. In the case of meat meal C1, compounds of this group are distributed between the organic and aqueous phases. The reduced lignin content of the algae resulted in a reduced phenol production during the conversion test.

Algae consists of carbohydrates, that were converted into O-heterocyclic compounds and ketons. The O-heterocyclic compounds formed during the meat meal C1 conversion could be formed during the protein decomposition.

3.7.3.4 ELEMENTAL COMPOSITION / PHYSICAL PROPERTIES

The pH value of both the organic and aqueous phases was in the basic region (≥7), which correlated with their high nitrogen content. This effect could be attributed to the presence of dissolved ammonia and/or lower amines, formed during the protein decomposition.

The HHV of a product correlates with its elemental composition. Thus, the organic phase of the algae conversion had the highest (C + H)/O ratio, providing the highest HHV compared with that of the other performed tests. Meat meal C1 showed a lower HHV compared with rapeseed cake conversion with H-ZSM-5 zeolite in the absence of the vapour upgrading section.

The algae produced an organic phase with a lower water content than the respective organic phase from the rapeseed cake conversion. The lower oxygen content of algae and its increased oil content had a beneficial effect in the final organic product, resulting in less water content of both organic and aqueous phases.

The meat meal C1 produced more water in the organic product compared with that of the rapeseed cake conversion. That could explain the increased solubility of N-heterocyclic compounds in the organic phase when the meat meal C1 was converted.

3.8 ENERGY BALANCE

The mass and energy flows of the KNV laboratory scale process are depicted in the Figure below:

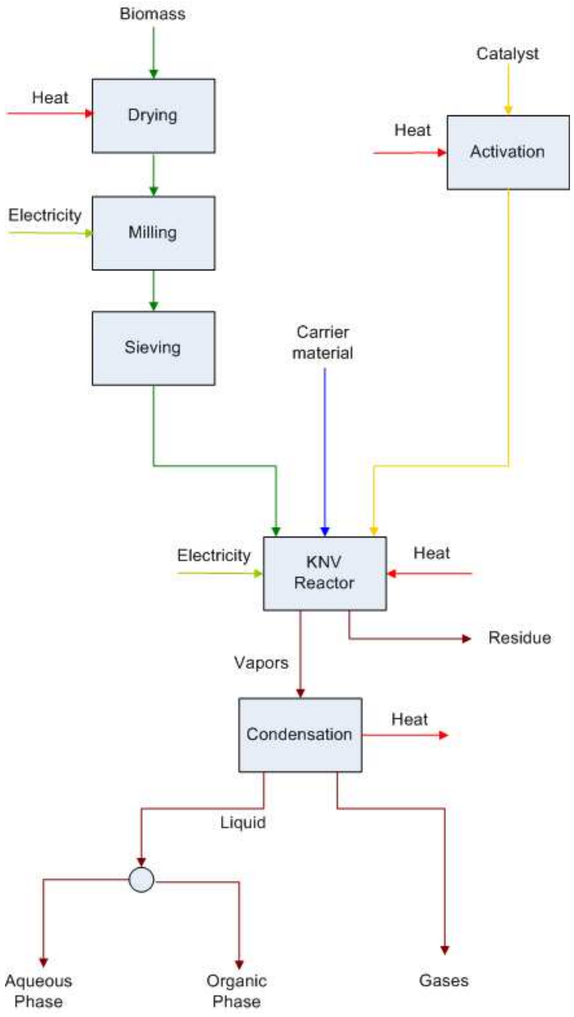


Figure 3-14. Mass and energy flows of the KNV laboratory process

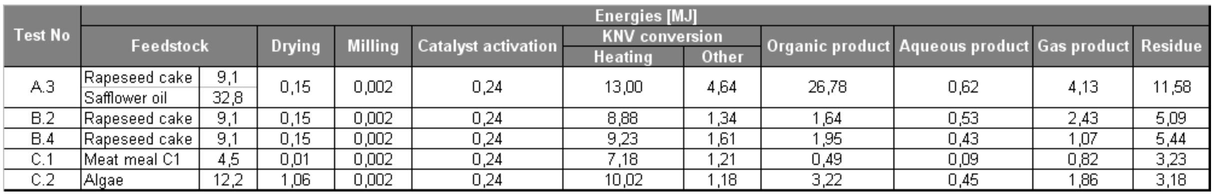
Sieving was performed manually during the laboratory tests preparation.

The energy balance of the following tests, performed at 400 ℃, was calculated: (1) the co-conversion of rapeseed cake and safflower oil with H-ZSM-5 zeolite [A.3], (2) the separate rapeseed cake conversion with H-ZSM-5 zeolite [B.2], (3) the separate rapeseed cake conversion with H-ZSM-5 zeolite in the presence of the vapour upgrading section [B.4], (4) the meat meal C1 conversion with H-ZSM-5 zeolite [C.1] and (5) the algae conversion with H-ZSM-5 zeolite in the presence of the vapour upgrading section [C.2].

The energy balance calculation of the KNV laboratory process was based on the higher heating values of the feedstock and products as well as the energy consumption during the biomass pre-treatment, catalyst activation and the catalytic conversion step. Devices for measuring the energy consumption were used during the test performance. The higher heating values of feedstocks and products were calculated by the prediction model developed by Boie, based on their elementary composition (see Annex). The total energy efficiency of the KNV laboratory process was calculated as the ratio of the useful energy (energy content of products) divided by the energy consumed (energy content of feedstocks, heat and electricity). The total energy efficiency of the process (from feedstock to biofuel production) could be increased by using the gas product of the KNV conversion to generate heat for the reactor.

The energy consumption during the selected KNV laboratory tests and the energy content of the products are presented in the following Table:

Table 3-14: Energy consumption and products energy content of the selected performed tests

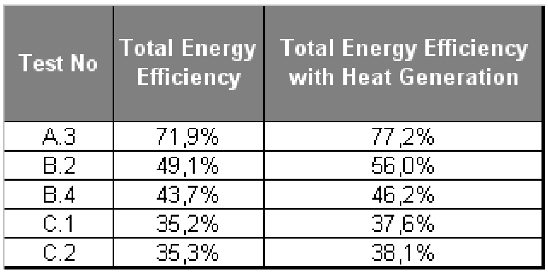


Test No	Energies [MJ]										
	Feedstock		Drying	Milling	Catalyst activation	KNV conversion		Organic product	Aqueous product	Gas product	Residue
						Heating	Other				
A.3	Rapeseed cake	9,1	0,15	0,002	0,24	13,00	4,64	26,78	0,62	4,13	11,58
	Safflower oil	32,8									
B.2	Rapeseed cake	9,1	0,15	0,002	0,24	8,88	1,34	1,64	0,53	2,43	5,09
B.4	Rapeseed cake	9,1	0,15	0,002	0,24	9,23	1,61	1,95	0,43	1,07	5,44
C.1	Meat meal C1	4,5	0,01	0,002	0,24	7,18	1,21	0,49	0,09	0,82	3,23
C.2	Algae	12,2	1,06	0,002	0,24	10,02	1,18	3,22	0,45	1,86	3,18

Due to the low material quantity, the energy required for the feedstock milling and the catalyst activation was equal for all experiments. The co-conversion test resulted in organic, gas and residue products with significant energy contents. The organic product of the algae conversion had a high energy content compared with separate rapeseed cake conversions and meat meal C1 conversion.

The energy efficiencies of the selected KNV laboratory tests are presented in the Table below:

Table 3-15: Energy efficiencies of the selected performed tests



Test No	Total Energy Efficiency	Total Energy Efficiency with Heat Generation
A.3	71,9%	77,2%
B.2	49,1%	56,0%
B.4	43,7%	46,2%
C.1	35,2%	37,6%
C.2	35,3%	38,1%

Both the total energy efficiency and the total energy efficiency with heat generation of the performed tests increased by the following order: C.1 < C.2 < B.4 < B.2 < A.3. The higher the energy content of the gas product, the higher the difference between the total energy efficiency and the total energy efficiency with heat generation.

The co-conversion test showed significantly higher energy efficiency compared with all other tests. This could be attributed to the high energy content of its KNV products. Comparing the two separate rapeseed cake conversion tests, the gas produced in the absence of the vapour upgrading section had an increased energy content, which resulted in an increased energy efficiency of this test. The algae drying required a significant amount of thermal energy. Although its products energy contents were similar to those of the separate rapeseed cake conversion in the presence of the vapour upgrading section, the energy efficiency of this test was significantly reduced.

4 FEASIBILITY STUDY

This chapter will present the results of the feasibility study for the upscaling of the KNV laboratory process into a KNV pilot plant.

To perform the feasibility study the following steps were followed: (1) research on the framework of the concept by identifying the present conditions concerning the policy, funding, technoeconomic and social framework, (2) performance of the technical design, (3) performance of the cost assessment and (4) performance of the economical evaluation.

The feasibility study for the pilot plant is condition-specific, in terms of raw materials, auxiliaries and process design. For this study, algae were selected as a raw material and the use of a vapour upgrading section was selected for the reactor set-up of the pilot plant.

4.1 RESEARCH ON THE FRAMEWORK

4.1.1 POLICY FRAMEWORK

According to the latest greenhouse gas emissions inventory of the Federal Environmental Agency, Austria emitted 78.96 million tons CO_2-equivalent in the Kyoto base year 1990. This value covers all greenhouse gases within the scope of the Kyoto Protocol. For Austria, the 13% reduction of greenhouse gases in the Kyoto commitment period 2008-2012 translates into a target value of about 68.69 million tons CO_2-equivalent. Compared with the 1990 figures, this is a reduction by 10.27 million tons CO_2-equivalent. The Austrian industry and transportation sectors are responsible for half of the energy consumption (European Technology Platform for Zero Emission Fossil Fuel Power Plants, 2009).

On 4 November 2004, the Biofuel Directive was transposed into Austrian national law with an amendment to the Fuel Ordinance. This amendment stipulates that all companies that put fuels in circulation (e.g. Österreichischen Mineralölverwaltung (OMV)) must, from 1 October 2005, replace 2.5% of the total fuel energy by biofuels. From 2007 this percentage will increase to 4.3% and in 2008 the target of 5.75%, as stipulated in the Directive, will have to be achieved. Together with the amendment to the Fuel Ordinance, the Mineral Oil Act has been revised. Accordingly, tax concessions will be granted for fuels with a biofuel share of at least 4.4%. However, to be able to profit from the tax concessions, the fuel must also be sulphur-free (less than 10 mg sulphur per kg of fuel) (Environmental Agency Austria, 2009). As shown from all the above, the european and local policy framework in Austria promotes the production and use of biofuels across the country.

4.1.2 FUNDING FRAMEWORK

The EU focus on the biofuel penetration in the energy market has forced country-members to establish funding and economic incentives for biofuel production companies. On a national level, these incentives differ from country to country, but usually follow two directions: (a) state funding in the form of loan with favourable terms for an important part of the total investment (up to 80%) and/or (b) tax exemption up to 100% of the profits. The rest of the money for the total investment has to be supplied by private investors.

On an international level, the Austrian Ministry of Transport, Innovation and Technology has been running the programme IV2Splus – “Intelligent Transport Systems and Services plus”. This programme focuses on expanding the excellence in research and development (R&D) through stronger international embedding of successfully established national R&D competences, with the goal of increased integration of these competences into international, industrial, value-creation chains (Austrian Federal Ministry for Transport, Innovation and Technology, 2009).

Either of these two options could supply the necessary funding for the erection and operation of a biofuel pilot plant in Austria.

4.1.3 TECHNOECONOMIC FRAMEWORK

As it was presented earlier in the results of Chapter 3, the use of algae as feedstock for the KNV process appears to have a good potential, due to its high liquid product yield, the high abundance of aliphatic hydrocarbons and the low oxygen content of the organic phase.

The algae cultivation system advantages lie: (a) on their high productivity potential, (b) on the ability to use otherwise unsuitable water and land resources, (c) on the ability to integrate waste treatment and (d) on the enhanced fuel production per area, compared with that of other biomass sources. Many of the approximately 50000 algal species can grow in brackish and saltwater. This means that the algae technology will not put additional demand on freshwater supplies needed for domestic, industrial and agricultural use. The ocean will become the ultimate sink for the anthropogenic CO_2. The unique ability of algae to grow in saline water means that we can target areas of a country which are coastal arid and/or in which saline groundwater supplies prevent any other useful application of water or land resources. The goal is to mitigate CO_2 into energy and/or to permanently sequester the biomass (and thus the CO_2) with the production of biofuels and biochemicals (Thomsen, 2008).

The organic product of the KNV pilot plant has to be post-treated to meet fuel standards before it is sold in the liquid fuel market. This could be done in conventional refineries, that are already equipped with the infrastructure for such treatments (e.g. desulphurization). Additionally, the aqueous product of the KNV pilot plant could be sold as raw material to chemical companies for the production of biochemicals.

The future global demand of biofuels is estimated to be approximately 250 billion liters by 2020, based on a scenario that looks at volume based targets that different regions may put in place by 2020 and how these targets might be met if 2^{nd} generation biofuels are available (E4tech, 2008). This means that the successful development and scaling up of a biofuel production technology can be sold around the world and bring profit to the inventors.

The location selection for the erection of the pilot plant is very important, since it has significant effect, not only on the economic stability of the investment plan, but also on the natural and social environment. Algae require high amounts of CO_2 during their cultivation. Therefore, the location of the algal bioreactor close to a CO_2 source, such as a power plant or plants which produce high amount of exhaust gases (e.g. cement industry), can be advantageous in terms of resource economy.

The main utility power plants in Austria are (European Technology Platform for Zero Emission Fossil Fuel Power Plants, 2009):

- EVN AG
- Verbund Austria Thermal Power GmbH & Co KG
- Wienstrom GmbH
- Energie AG Oberösterreich
- Linz Strom.

Energie AG, in Upper Austria, has shown interest in cooperating on a project for the industrial production of algal biomass, using CO_2 directly from the power plant emissions. The algae production site should be located close to the facilities of the Energie AG for the direct utilization of the CO_2 emissions. The KNV pilot plant should also be erected close to the algal biomass production area to avoid costly transportation of the raw material to the pilot plant location. This area appears to have sufficient infrastructure for plant erection and operation (road network, access to raw and auxiliary materials, labour resources), because it is close to the plant facilities of the Energie AG. Since the produced biofuel, which has higher bulk density than the algal feedstock, has to be sent to a conventional refinery for post-treatment, it could be transferred to the local installations of Rohöl-Aufsuchungs AG (RAG) in Gampern (Upper Austria) and then be transported either by pipeline or via railway tank cars to the Schwechat refinery of OMV (Rohöl-Aufsuchungs AG, 2009).

4.1.4 SOCIAL FRAMEWORK

The last years, there has been increased awareness of the public opinion concerning the global environmental problems and the greenhouse gas emissions. Locals have been experiencing weather extremes around the year, which affect the agricultural and fauna balances and cause environmental distructions, such as floods and droughts. Measures and investment plans aiming to reduce emissions in an area where an intensive air-polluting plant is located will be welcomed by local authorities and residents.

4.2 TECHNICAL DESIGN

The technical design of the KNV pilot plant was the key step of the feasibility study, since this was the core, based on which the cost assessment and the economic evaluation of the investment plan were designed. The larger size of the pilot plant compared with that of the laboratory unit provided the possibility for design changes, to assure higher material and energy efficiency.

In principal, the technical design should be based on simplicity, efficiency, sustainability and safety. Additionally, the design should provide flexibility for future changes, depending on the optimization requirements and/or future demands of the process. The selected equipment has to be reliable, economic and safe. The cost of operation and maintenance should not be high, the emissions should be controllable and the energy consumption should be minimized. The use of continuous operation equipment could decrease the labour costs, since there will be no demand for repeated loading and unloading of materials, but the investment costs would increase.

The KNV pilot plant would be operating in series with the algae production site close to Energie AG. The area of the algae production pilot plant was planned to be 10000 m^2. Smaller algae production areas would create challenges in the profitability of the investment plan for the erection and operation of the KNV pilot plant. The algae productivity can vary according to the bioreactor design. The maximum productivity reported in literature reference was 1.5 kg dry algae/m^3/d (Sanchez Miron et al., 1999) and for this study, this productivity was used. Assuming an algal reactor volume of 10000 m^3, that would yield 15000 kg dry algae/d, which would then be sent to the KNV pilot plant for conversion.

4.2.1 PRE-TREATMENT: ALGAE

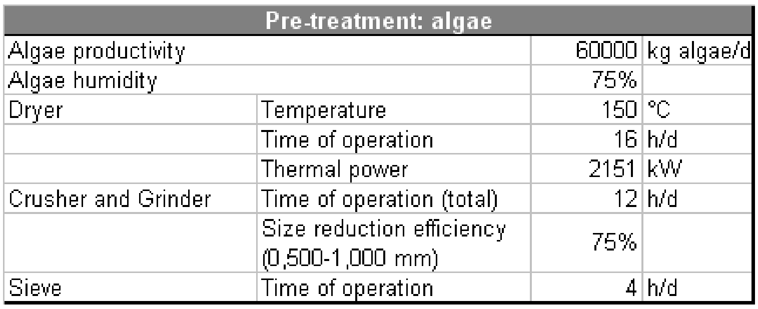
Harvested algae have to be pre-treated before they reach the conversion reactor. The pre-treatment procedure includes a drying process, a size reduction process and a screening process. As demonstrated in the laboratory scale tests, the desirable humidity level of the reactor feedstock was <10% and the desirable size fraction was 0.500-1.000 mm.

There is a wide variety of dryers, such as tray dryers, screen-conveyor dryers, tower dryers, rotary dyers, screw conveyor dryers, fluid bed dryers, spray dryers, thin film dryers and drum dryers. The algae consist of an important amount of humidity. Depending on the algae harvesting method, the harvested algae may be in the form of a thick paste or even in the form of a highly concentrated solution. The types that appear to be suitable for the specific application of the KNV pilot plant are: (1) the screw conveyor dryer (suitable for pasty materials), (2) the drum dryer (suitable for pasty materials and solutions). Spray dryers and thin film dryers could also be used. But in the first case, this equipment is complicated and it does not have a high efficiency when it is used only as dryer (efficiency is increased when it is also used as an evaporator, crystallizer, size reduction unit and grader). In the second case, this equipment is relatively expensive and has a relatively low surface for thermal treatment (McCabe, 2001).

The comminuting equipment is classified into crushers, grinders, ultrafine grinders and cutters. Primary crushers can process big pieces of minerals (e.g. from mines) and break them into pieces of 150-200 mm size. A secondary crusher can reduce the size of these particles to 6 mm. Grinders can produce particles up to 74 μm, while ultrafine grinders 1-50 μm. During the laboratory experiments, the wet algae paste was fed into a batch laboratory dryer and the dried paste was in the form of big pieces (~150 mm) of strong thick texture. The size of these pieces indicated that it would be necessary to combine a secondary crusher and a grinder in series to produce algae particles with 1 mm maximum diameter. Different types of crushers exist, such as jaw crushers, gyratory crushers and roll crushers. Roll crushers are secondary crushers that can give a product with 1-12 mm particle size. Additionally, different types of grinders exist, such as hammer mills, impactors, rolling-compression machines and attrition mills. Very often the comminuting process takes place in a closed system, where a comminuting equipment and a separator are connected in such a way that larger size particles are recycled. In this case, energy has to be spent on the operation of transporters and separators, but the reduction in the energy consumption of closed systems in comparison with that of open systems can reach up to 25%. The energy cost is a very important point during comminuting processes, therefore it is important to select the most suitable equipment and the parameters that can regulate this cost. The size reduction is one of the less energy efficiency processes, since less than 1% of the provided energy is used for the new surface production. The rest is consumed during equipment operation and as heat losses (McCabe, 2001).

The estimated parameters of the algae pre-treatment process are summarized in the following Table:

Table 4-1: Estimated parameters of the algae pre-treatment process



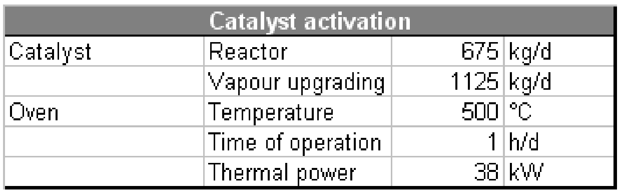
Pre-treatment: algae			
Algae productivity		60000	kg algae/d
Algae humidity		75%	
Dryer	Temperature	150	°C
	Time of operation	16	h/d
	Thermal power	2151	kW
Crusher and Grinder	Time of operation (total)	12	h/d
	Size reduction efficiency (0,500-1,000 mm)	75%	
Sieve	Time of operation	4	h/d

4.2.2 PRE-TREATMENT: CATALYST

The catalyst has to be activated by calcination at 500 °C for 1 h in an oven, before it is used during the conversion. During the laboratory tests, catalyst in powder form was mixed with the algae and was fed into the reactor. Additionally, catalyst in extruded form was added in the vapour upgrading section. The diameter of the extruded catalyst used in the laboratory tests was 2 mm. The regeneration of the catalyst in powder form was difficult, due to the fact that the used catalyst was mixed with the residue. After regeneration, the residue produced ash in powder form. The separation of the regenerated catalyst from the ash was very challenging. Therefore, it was decided that catalyst in extruded form would be mixed with the algal feedstock in the KNV pilot plant. The catalyst collection and regeneration are very important, since the operational costs can be significantly reduced via catalyst recycling. The extruded catalyst employment was expected to enhance the transport phenomena in the reactor. Consequently, a 100% increase in the catalyst quantity was utilized and mixed with the algae. As a result, the catalyst in the reactor will be equal to 6% wt. of the algae, instead of 3% wt. that was used during the laboratory tests.

The estimated parameters of the catalyst pre-treatment process are summarized in the following Table:

Table 4-2: Estimated parameters of the catalyst pre-treatment process



Catalyst activation			
Catalyst	Reactor	675	kg/d
	Vapour upgrading	1125	kg/d
Oven	Temperature	500	°C
	Time of operation	1	h/d
	Thermal power	38	kW

4.2.3 CONVERSION

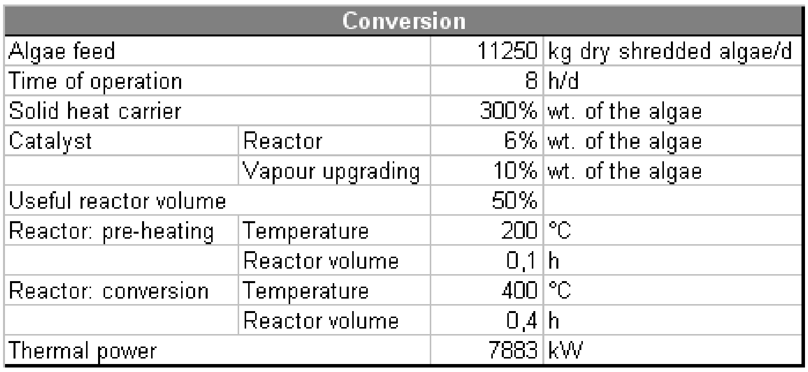
The algae, the catalyst and the solid heat carrier were mixed before they entered the reactor. The dry solid material mixing requires more energy than the mixing of liquids. Unlike the liquid material mixing, where a completely homogenized liquid phase can be produced, the solid material mixing produces two or more easily distinctive phases. They are considered “well mixed” when the ratio of the mixed particles are in the range of a specified value, defined by the engineers. There are four types of mixers suitable for dry solid particles: (a) ribbon blenders, (b) internal screw mixers, (c) tumbling mixers and (d) impact wheels. The internal screw mixers mix in a slower rate than the ribbon blenders, but the energy consumption is lower (McCabe, 2001).

The reactor is the main component of the conversion system. The biomass conversion is an endothermic process. For this reason, the heat transfer towards the reactor has to be efficient. The heat can be transferred conventionally, via convection from the heating medium and via conduction through the walls of the reactor. Alternatively, the heat can be transferred via induction. Two different design layouts were examined: (i) Design Layout A: with conventional reactor heating and (ii) Design Layout B: with induction reactor heating.

In both design layouts, the reactor of the pilot plant would be a continuous, horizontal, rotating, single screw reactor. Along the edge of the helix, sharp scrapers would be attached and would be touching the reactor shell. In this way, the inner surface of the reactor shell could be “cleaned” during the operation by carrying away the produced charcoal. The accumulation of this highly viscous charcoal residue would be responsible for regular maintenance. The residence time of the reactor could be regulated by the screw pitch and the rotation speed of the screw. A double screw could be used instead of a single, but the wear rate and solid attrition would be increased in this case. This effect is not desirable, since after regeneration the separation of the catalyst and the solid heat carrier from the charcoal ash would be more difficult, due to the fine particle size of the materials. The reactor would be divided into a pre-heating section (~200 ℃) and the actual conversion section (400 ℃) to increase the heat transfer rate . Due to the optimized engineering of the pilot plant, the mass balance could reach the following yields: (1) organic phase: 45%, (2) aqueous phase: 25%, (3) gas product: 15%, (4) residue: 15%. An opening at the bottom end of the tubular reactor would lead the residue to a collection tank. At the upper end of the tubular reactor, an opening would lead the gases and vapours at the vapour upgrading section, via the application of vacuum. The vapour upgrading section would be a vertical tubular reactor, where the catalyst pellets would be placed in a fixed bed. Due to the limited catalytic activity, a second vapour upgrading section would be placed in parallel with the first. When the catalytic activity would be significantly reduced, the first section would be isolated and the second section would be connected in series with the reactor and vice versa.

The estimated parameters of the conversion process are summarized in the following Table:

Table 4-3: Estimated parameters of the conversion process



Conversion			
Algae feed		11250	kg dry shredded algae/d
Time of operation		8	h/d
Solid heat carrier		300%	wt. of the algae
Catalyst	Reactor	6%	wt. of the algae
	Vapour upgrading	10%	wt. of the algae
Useful reactor volume		50%	
Reactor: pre-heating	Temperature	200	°C
	Reactor volume	0,1	h
Reactor: conversion	Temperature	400	°C
	Reactor volume	0,4	h
Thermal power		7883	kW

After the vapour upgrading section, a condenser would be applied to condense the mixture of organic and aqueous vapours from ~360 ℃ to ~70 ℃. The condensation rate of these vapours would be significantly reduced, since non-condensable gases would also be present in the mixture. The condensers suitable for such applications should be placed vertically instead of horizontally. Vapours should be condensed inside the tubes, while the cooling medium should flow inside the shell (McCabe, 2001).

The non-condensable gases would exit the system via the vacuum pump. Due to the fact that slight vacuum would be used during the operation (0.9 bar absolute pressure) a side channel blower could be utilized, since its purchasing cost would be significantly lower compared with other types of vacuum pumps.

All three products of the conversion process would be collected in storage tanks. The gas product would be collected in a volumetric tank. The mixture of condensed vapours (liquid product) would be collected in a vessel and be left to rest. The different density of the liquid compounds would create two immiscible phases which could then be easily separated. Each phase (organic and aqueous) would be put in different storage tanks.

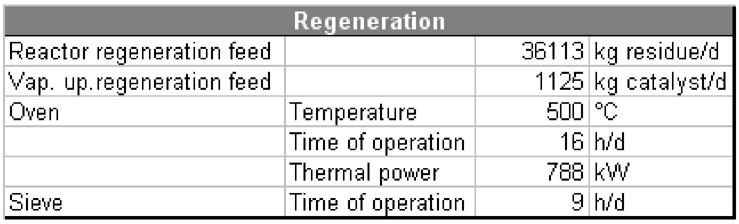
4.2.4 REGENERATION

The regeneration of the reactor residue and the vapour upgrading catalyst would be performed in the same oven used for the catalyst activation process. Both materials would be regenerated at 500 ℃ for 16 h. During the regeneration process, all organic depositions would be oxidized in a controllable way, by regulating the atmosphere and temperature of the regeneration chamber. The charcoal oxidation is an exothermic reaction, which requires significant amount of thermal energy at the reaction offset. It was assumed that the regeneration efficiency of the reactor catalyst could be 70% and it could be used for 15 additional times. The regeneration efficiency of the vapour upgrading catalyst could be 100% and it could be used for 15 additional times.

After the residue regeneration, the mixture of the solid heat carrier, the algal ash and the catalyst would exit the oven. This mixture would be guided to the screening equipment to separate the fractions of powder (<0.5 mm), solid heat carrier (0.5-2.0 mm) and catalyst (>2.0 mm). Due to increased attrition forces inside the screw reactor during operation, some material losses would be expected, because of a size reduction that would lead to powder formation. These losses were considered negligible for the present calculations.

The estimated parameters of the regeneration process are summarized in the following Table:

Table 4-4: Estimated parameters of the regeneration process



Regeneration			
Reactor regeneration feed		36113	kg residue/d
Vap. up.regeneration feed		1125	kg catalyst/d
Oven	Temperature	500	°C
	Time of operation	16	h/d
	Thermal power	788	kW
Sieve	Time of operation	9	h/d

4.2.5 SAFETY

Industries that deal with powders, liquids and gases that can create explosive mixtures in the atmosphere must take necessary measures to avoid such incidents. The EN 1137 regulation demands that such risks should be eliminated or minimized using three principles: (i) prevention by avoiding explosive atmospheres, (ii) prevention by avoiding effective ignition sources and (iii) protection by limiting the effects of explosions (Riskman, 2009).

The ATEX application directive affects a vast number of companies, such as those which process seeds, feedstuff or wood, use coating machinery or produce fireworks or biogas (Grontmijcarlbro, 2009). For powders, the probability of ignition, especially from electrostatic discharges, has to be examined. Consideration must be given to the movement of material after drying, where fine dust can be produced by attrition. Dust collectors can become high risk areas for fire or explosion. For liquids/gases, their handling and use as fuels requires Hazardous Area Classification and Basis of Safety definition according to the latest European Standards. Often a large number of wastes (e.g. ash) are flammable and their disposal must be handled with the necessary safety measures (Chilworth Global, 2009). The minimization of ignition sources in closed areas where materials are handled is a common practice for preventing fires and explosions. Several process equipment types are classified according to the ATEX directive for the conditions under which they can operate safely. An increase in their ATEX classification is followed by an increase in their purchasing cost.

The ATEX directive advises that the affected workplaces must implement an extended workplace assessment, reviewing the potentially explosive areas in the company and comprising, among other things, a full-scale safety analysis, a risk assessment and personnel training plans (Grontmijcarlbro, 2009). As expected, such studies increase the investment cost for the erection of a pilot plant, but are still necessary for the safe operation of the production site. For the present calculations, the cost of performing such studies was considered negligible for reasons of simplicity.

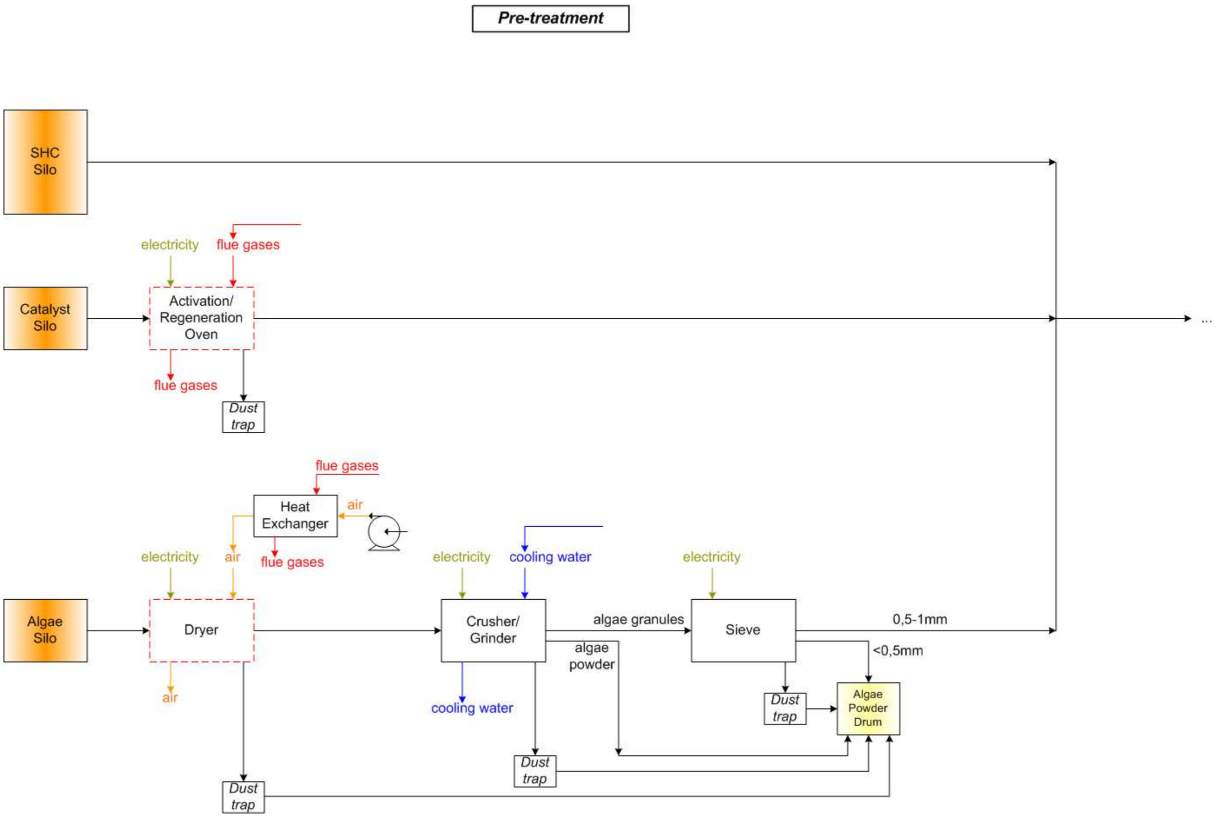
4.2.6 ENVIRONMENT

The removal of solid particles dispersed in gases (e.g. flue gases) is very important and crucial in environmental technology. The gas emissions from production plants transfer particles towards the atmosphere, which originate either from combustion or from the production processes that take place. Cyclones and electrofilters are very often used, especially in industries that are significant producers of gas streams containing solid particles, such as the cement industry, the industry of inorganic acids and metallurgies. Due to the high investment cost of this equipment, for the present calculations on the KNV pilot plant it was assumed that the produced fume gases contain a low amount of solid particles.

4.2.7 DESIGN LAYOUT A

For the Design Layout A, the reactor would be made out of stainless steel. A burner would be used to heat up the activation/regeneration oven (500 ℃) and the reactor (400 ℃). The burner would be able to operate with two different types of gas fuels: (a) with natural gas from the grid and (b) with the gas product of the algae KNV conversion. The gas product would contain corrosive compounds (e.g. H_2S), therefore the burner might require more frequent maintenance. The gas burner would have a thermal capacity of 8000 kW. Double walled equipment (reactor, oven) would be used, since their content (algae, catalyst) should not be in direct contact with the flue gases.

The proposed flowsheet of the KNV pilot plant for the algae conversion into liquid biofuel is presented in the following Figure. The mass flow of the materials (algae, solid heat carrier, catalyst) is marked in black, the flow of the auxiliary utilities (electricity, flue gases, air, cooling water) is marked in colour, the storage vessels are marked with patterned fill and the processes that require heat are marked with dashed red lines.



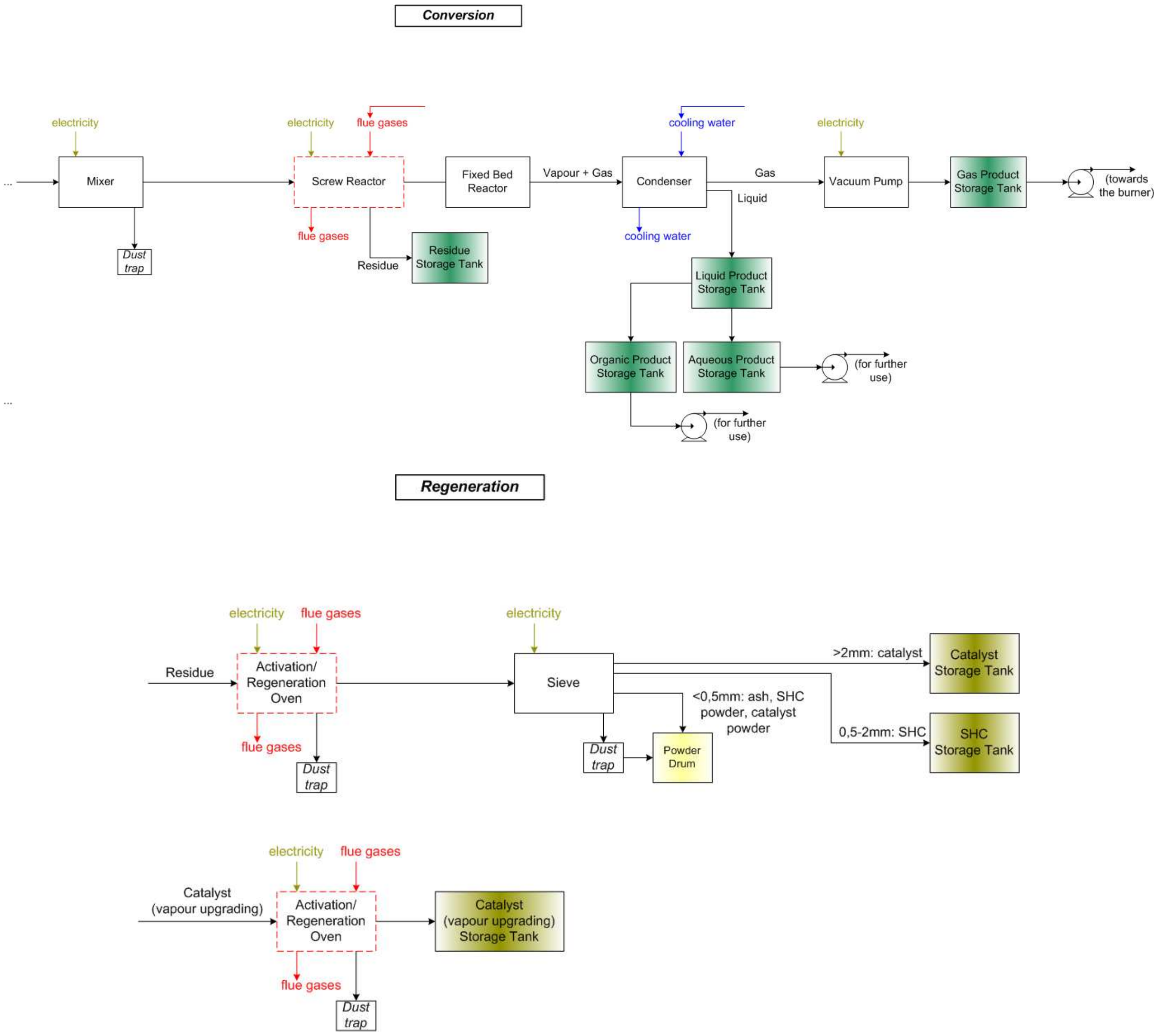
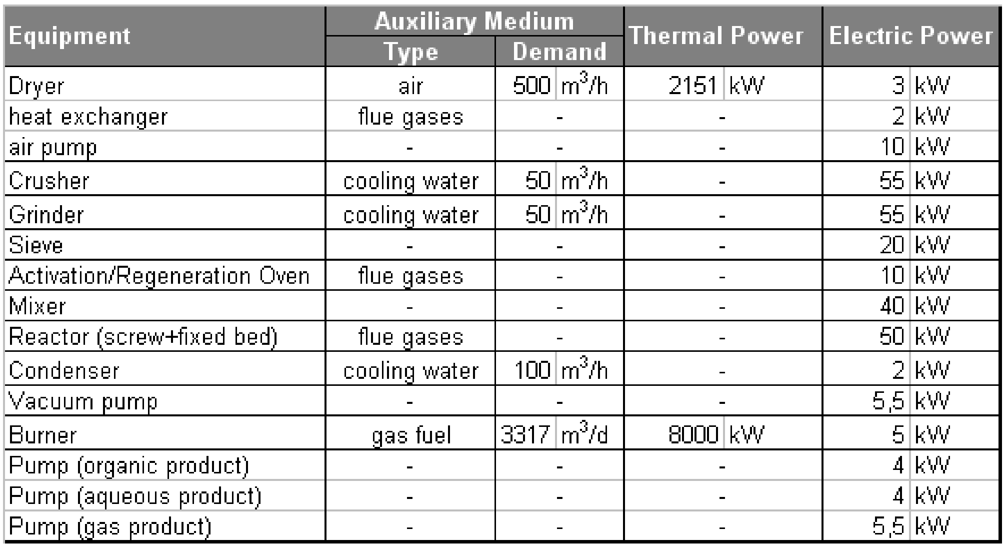


Figure 4-1. KNV pilot plant flowsheet for the Design Layout A

The list of the necessary equipment and their characteristics is presented in the following Table:

Table 4-5: Necessary equipment and their characteristics for the Design Layout A



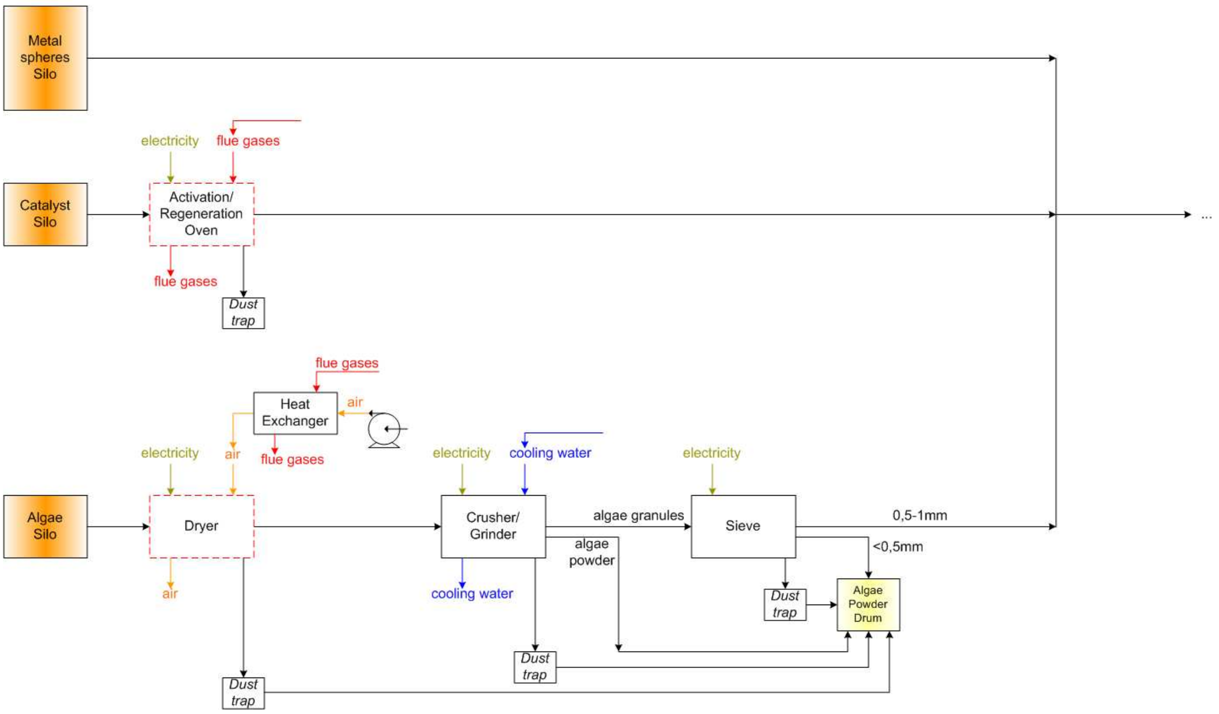
Equipment	Auxiliary Medium		Thermal Power	Electric Power
	Type	Demand		
Dryer	air	500 m^3/h	2151 kW	3 kW
heat exchanger	flue gases	-	-	2 kW
air pump	-	-	-	10 kW
Crusher	cooling water	50 m^3/h	-	55 kW
Grinder	cooling water	50 m^3/h	-	55 kW
Sieve	-	-	-	20 kW
Activation/Regeneration Oven	flue gases	-	-	10 kW
Mixer	-	-	-	40 kW
Reactor (screw+fixed bed)	flue gases	-	-	50 kW
Condenser	cooling water	100 m^3/h	-	2 kW
Vacuum pump	-	-	-	5,5 kW
Burner	gas fuel	3317 m^3/d	8000 kW	5 kW
Pump (organic product)	-	-	-	4 kW
Pump (aqueous product)	-	-	-	4 kW
Pump (gas product)	-	-	-	5,5 kW

4.2.8 DESIGN LAYOUT B

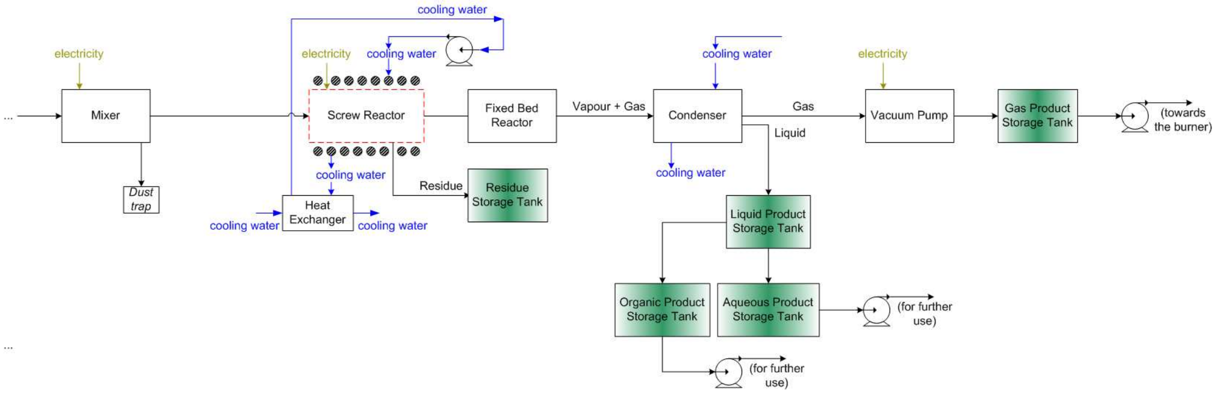
For the Design Layout B, the reactor would be made out of non-metal material that could stand high temperatures, such as ceramic. The reactor would be heated up by using an induction generator, which would be creating an induction field around the screw reactor. The induction heating system would consist of the following components: the induction generator, the heating coil and the heat exchanger for the cooling medium, which would be cooling water in this case. The cooling medium would be pumped in a closed circuit. The heat exchanger could be air/water or water/water. For this application, a water/water heat exchanger could be used. Metal spheres (4 mm) would be added inside this reactor to directly heat up the loaded feedstock, rather than the walls of the reactor. In this way, the temperature profile inside the feedstock would be more homogeneous and local overheating would be avoided. Still, it is expected that the investment cost of an induction heating system would be higher than that of a conventional heating system.

The proposed flowsheet of the KNV pilot plant for the algae conversion into liquid biofuel is presented in the following Figure. The mass flow of the materials (algae, solid heat carrier, catalyst) is marked in black, the flow of the auxiliary utilities (electricity, flue gases, air, cooling water) is marked in colour, the storage vessels are marked with patterned fill and the processes that require heat are marked with dashed red lines:

Pre-treatment



Conversion



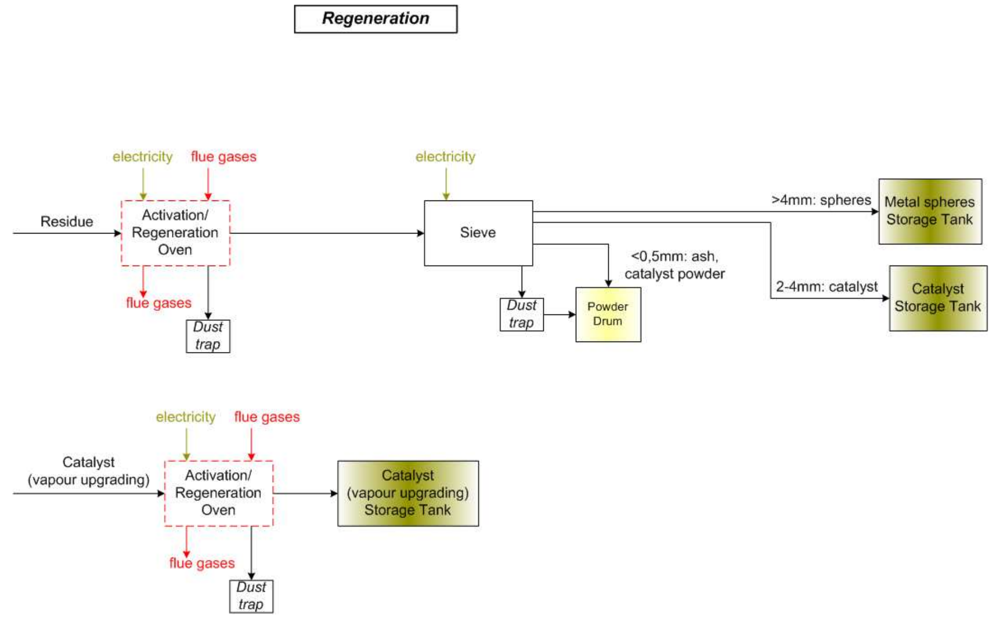
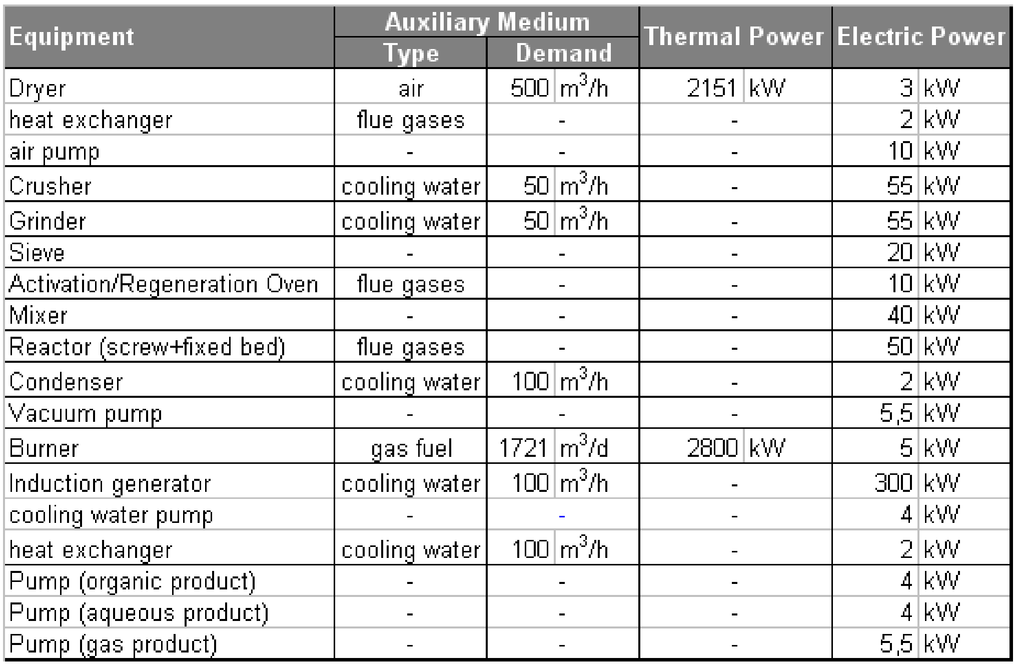


Figure 4-2. KNV pilot plant flowsheet for the Design Layout B

The list of the necessary equipment and their characteristics is presented in the following Table:

Table 4-6: Necessary equipment and their characteristics for the Design Layout B



Equipment	Auxiliary Medium		Thermal Power	Electric Power
	Type	Demand		
Dryer	air	500 m^3/h	2151 kW	3 kW
heat exchanger	flue gases	-	-	2 kW
air pump	-	-	-	10 kW
Crusher	cooling water	50 m^3/h	-	55 kW
Grinder	cooling water	50 m^3/h	-	55 kW
Sieve	-	-	-	20 kW
Activation/Regeneration Oven	flue gases	-	-	10 kW
Mixer	-	-	-	40 kW
Reactor (screw+fixed bed)	flue gases	-	-	50 kW
Condenser	cooling water	100 m^3/h	-	2 kW
Vacuum pump	-	-	-	5,5 kW
Burner	gas fuel	1721 m^3/d	2800 kW	5 kW
Induction generator	cooling water	100 m^3/h	-	300 kW
cooling water pump	-	-	-	4 kW
heat exchanger	cooling water	100 m^3/h	-	2 kW
Pump (organic product)	-	-	-	4 kW
Pump (aqueous product)	-	-	-	4 kW
Pump (gas product)	-	-	-	5,5 kW

4.3 COST ASSESSMENT

For the cost assessment, a Preliminary Estimate was performed. Such estimates are usually used to assist the decision making process and to integrate an investment plan to the budget of a company. A variety of information was needed, such as mass and energy balances, a list of necessary equipment, a pilot plant layout and a pilot plant location. Some of the investment elements (piping, insulation, electrical, e.t.c.) were estimated as a percentage of the basic equipment cost, but others were analytically calculated (i.e. equipment). The possibility of error in such estimates is less than ±20% (Lipowatz-Kremezi, 2003).

The total investment for the erection and operation of the pilot plant consists of two main components: the fixed investment and the turnover capital. The fixed investment is the required amount of money needed for the construction of the main and auxiliary installations of a plant. The turnover capital is the necessary amount of money needed to cover the operational expenses of the plant (Lipowatz-Kremezi, 2003).

4.3.1 FIXED INVESTMENT

The equipment investment cost is a key element of the fixed investment, based on which the total fixed investment cost can be calculated. When referring to the equipment investment cost, there is a distinction between the purchasing cost, the delivery cost and the installation cost. In the present calculations, the delivery cost was integrated into the purchasing cost. The installation cost can be calculated as a percentage of the purchasing cost (Lipowatz-Kremezi, 2003).

The equipment purchasing cost for both Design Layouts are depicted in the following Table:

Table 4-7: Equipment purchasing cost for the Design Layout A and B

Equipment	Purchasing Cost [€]	
	Design Layout A	Design Layout B
Dryer	140321	140321
heat exchanger	9355	9355
air pump	9355	9355
Crusher	70160	70160
Grinder	70160	70160
Sieve	32741	32741
Activation/Regeneration Oven	70160	70160
Mixer	70160	70160
Reactor (screw+fixed bed)	140321	140321
Condenser	28064	28064
Vacuum pump	9355	9355
Burner	280641	93547
Induction generator	-	935470
cooling water pump	-	
heat exchanger	-	
Pump (organic product)	9355	9355
Pump (aqueous product)	9355	9355
Pump (gas product)	9355	9355
Total purchasing cost:	958857	1707233

The fixed investment includes a series of direct or indirect costs. Different methodologies can be used for the calculation of the total fixed investment cost. For the present study, the Lang methodology was applied. According to this, the total fixed investment cost can be calculated as (Lipowatz-Kremezi, 2003):

$$C_F = [C_E + (\Sigma f_j C_E)] f_I$$

where C_F: the fixed investment cost for the plant

C_E: the purchasing cost for all the plant equipment

f_j: a coefficient per cost category to estimate the cost of piping, monitoring/control, electrical installation, building, land preparation, auxiliary installations and land investment

f_I: a coefficient to estimate the indirect costs (design and supervision, construction labour costs, contractor costs, unexpected expenses)

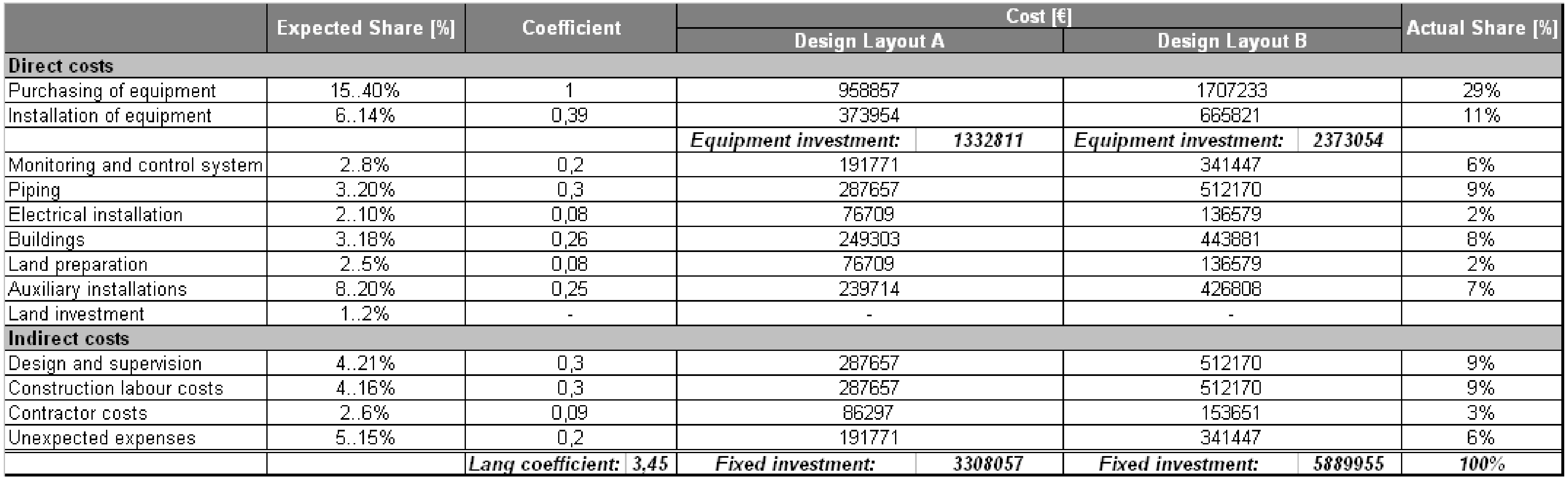
The equation above can be written in the following form:

$$C_F = f_L \, C_E$$

where $f_L = [1 + (\Sigma f_j)] f_I$, is the Lang coefficient

The calculation of the Lang coefficient was performed for solid/fluid processing of a pilot plant, with medium scale automated control, mostly located in an indoor construction, without important additions in auxiliary intallations, on the grounds that the KNV pilot plant will be closely located to the Energie AG plant. The following Table presents the basic cost factors of the fixed investment, their estimated coefficients according to the Lang methodology and their actuall cost in Euros (Lipowatz-Kremezi, 2003):

Table 4-8: Basic cost factors of the fixed investment and their coefficients over the equipment purchasing cost (Lipowatz-Kremezi, 2003)



	Expected Share [%]	Coefficient	Cost [€]		Actual Share [%]
			Design Layout A	Design Layout B	
Direct costs					
Purchasing of equipment	15..40%	1	958857	1707233	29%
Installation of equipment	6..14%	0,39	373954	665821	11%
			Equipment investment: ***1332811***	*Equipment investment:* ***2373054***	
Monitoring and control system	2..8%	0,2	191771	341447	6%
Piping	3..20%	0,3	287657	512170	9%
Electrical installation	2..10%	0,08	76709	136579	2%
Buildings	3..18%	0,26	249303	443881	8%
Land preparation	2..5%	0,08	76709	136579	2%
Auxiliary installations	8..20%	0,25	239714	426808	7%
Land investment	1..2%	-	-	-	
Indirect costs					
Design and supervision	4..21%	0,3	287657	512170	9%
Construction labour costs	4..16%	0,3	287657	512170	9%
Contractor costs	2..6%	0,09	86297	153651	3%
Unexpected expenses	5..15%	0,2	191771	341447	6%
		Lang coefficient: ***3,45***	*Fixed investment:* ***3308057***	*Fixed investment:* ***5889955***	***100%***

As expected, the fixed investment of the Design Layout B was significantly higher than that of the Design Layout A (almost twice as high).

4.3.2 TURNOVER CAPITAL

For the calculation of the operational cost (production cost), the activity degree of the plant should be defined. In every plant the operation is stopped for some days per year for repair and/or maintenance. Consequently, the activity degree rarely exceeds the level of 90-95%. The mean activity degree in industry is approximately 80% (Lipowatz-Kremezi, 2003).

The breakdown of the total production cost is presented below:

Table 4-9: Breakdown of the total production cost (Lipowatz-Kremezi, 2003)

Total Production Cost - Breakdown						
Process Cost						
Direct Cost						
1	Raw material					
2	Auxiliary material					
	2a. for Production	2b. for Repair and Maintenance	2c. for Laboratory	2d. for By-product and Scrap Credit	2e. for Unexpected use	2f. for Rights
3	Supplies					
	3a. Electricity	3b. Natural gas	3c. Cooling water	3d. Air	3e. Gas nitrogen	3f. Silica gel
4	Labour					
	4a. Technicians	4b. Engineers	4c. Supervisor	4d. Maintenace technicians	4e. Maintenace supervisor	4f. Added labour costs
Fixed Cost						
1	Amortization					
2	Property Tax					
3	Insurance					
4	Rent					
5	Interest					
Expenses						
1	Doctor					
2	Insurance and Protection					
3	General Added Expenses					
4	General Payment Expenses					
5	Packing					
6	Restaurant					
7	Recreation					
8	First Aid Service					
9	Control Laboratories					
10	General Janitor					
11	Storage Installation					
General expenses						
Administration expenses						
1	Executive Salary					
2	Employee Salary					
3	Engineer Salary					
4	Office Maintenance					
5	Telecommunication					
Sales Expenses						
1	Sales shops					
2	Salesmen Expenses					
3	Courier					
4	Advertizing					
5	Technical Support					
Research and Development						

The added labour costs include dues, holiday bonus, day-off allowance and participation to profits. For the present calculation, the administration expenses were included as overhead charges in the hourly rate of engineers and technicians. It was assumed that the research and development expenses would be covered by Joanneum Research. The sales expenses were assumed to be insignificant, since the product could be sold to selected parties. Due to the fact that the pilot plant would be located close to the Energie AG plant, the process cost expenses could be minimized, as these provisions could be supplied by the nearby plant facility. Finally, it was assumed that the cost of the raw material would be insignificant, since the environmental regulations for the reduction of the CO_2 emmissions would motivate the establishment of a co-operation deal between the power plant and the KNV pilot plant.

Analyzing the production cost of a big number of chemical plants, different researchers have set forward simple or more complex models for the production cost calculation, using the cost of five basic parameters: the raw materials, the direct labour, the energy, the fixed investment and the sales expenses. The direct and indirect production expenses can be expressed as parts of these five basic parameters.

4.3.2.1 LABOUR COST

For the calculation of the labour cost, it was important to estimate the number of technicians and engineers per shift. The following scheme illustrates the time-plan for the processes of the KNV pilot plant and the predicted demand for employees (technicians and engineers) during the plant operation:

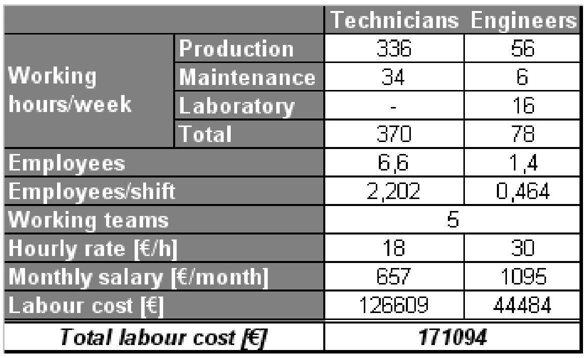
Table 4-10: Time-plan for the KNV pilot plant and predicted demand for employees

		Day	**Day 1**																							
		Hour	**6:00**	**7:00**	**8:00**	**9:00**	**10:00**	**11:00**	**12:00**	**13:00**	**14:00**	**15:00**	**16:00**	**17:00**	**18:00**	**19:00**	**20:00**	**21:00**	**22:00**	**23:00**	**0:00**	**1:00**	**2:00**	**3:00**	**4:00**	**5:00**
Weekly timeplan			■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
No	**Process**																									
1	*Drying*		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■								
2	*Crushing*																		■	■	■	■	■	■		
3	*Milling*																			■	■	■	■	■	■	■
4	*Sieving (feed)*																						■	■	■	■
5	*Activation Oven*		■																							
6	*Mixer*			■	■	■	■	■	■	■	■	■	■													
7	*Reactor*						■	■	■	■	■	■	■	■												
8	*Regeneration oven (residue , vap. up. catalyst)*														■	■	■	■	■	■	■	■	■	■	■	■
9	*Sieving (after regeneration)*																									
10	*Burner*		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■								
		Technicians:	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
		Engineers:					1	1	1	1	1	1	1	1												
	Maintenance: 34 h/week	Technicians: 1																								
	Maintenance: 6 h/week	Engineers: 1																								
	Lab: 16 h/week	Engineers: 1																								

It was assessed that the production of the KNV pilot plant would be stopped for 34 h/w to perform maintenance (80% degree of production activity), while the laboratory analysis of the products would require 16 h/w. It was assumed that the pilot plant would be operating 24 h/d, 7 d/w. The continuous operation of the plant would correspond to 8760 working h/y. Every working team would cover 40 h/w * 52 weeks/y = 2080 h/y. As a result, 8769 / 2080 = 4.21 working teams would be requested. Considering that each employee would require 4 weeks/y for holidays, every working team would cover 1920 h/y, consequently 8769 / 1920 = 4.56 working teams would be needed. Due to the existence of public holidays and the absence of employees from work due to medical reasons, it was decided that 5 working teams would be necessary, working 36.5 working h/week. Each employee would be receiving 14 salaries per year. The added labour costs (dues, holiday bonus) were estimated as 25% of the total labour cost calculation.

The following Table depicts the calculation of the total labour cost:

Table 4-11: Total labour cost calculation



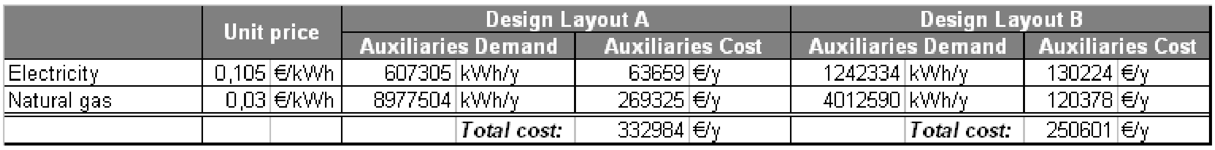
		Technicians	Engineers
Working hours/week	Production	336	56
	Maintenance	34	6
	Laboratory	-	16
	Total	370	78
Employees		6,6	1,4
Employees/shift		2,202	0,464
Working teams		5	
Hourly rate [€/h]		18	30
Monthly salary [€/month]		657	1095
Labour cost [€]		126609	44484
Total labour cost [€]		***171094***	

The labour cost was equal for both Design Layouts.

4.3.2.2 ENERGY AND AUXILIARY MATERIAL COST

The energy costs of both Design Layouts are displayed in the following Table:

Table 4-12: Energy cost calculation

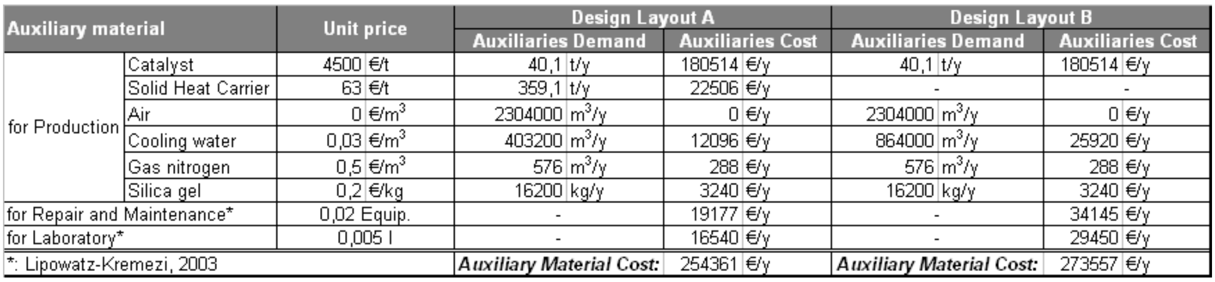


	Unit price	Design Layout A		Design Layout B	
		Auxiliaries Demand	Auxiliaries Cost	Auxiliaries Demand	Auxiliaries Cost
Electricity	0,105 €/kWh	607305 kWh/y	63659 €/y	1242334 kWh/y	130224 €/y
Natural gas	0,03 €/kWh	8977504 kWh/y	269325 €/y	4012590 kWh/y	120378 €/y
		Total cost:	332984 €/y	*Total cost:*	250601 €/y

The natural gas consumption is higher in the Design Layout A, but the electricity consumption is higher in the Design Layout B. The differences in their unit prices result in higher energy cost for the Design Layout A in comparison with the Design Layout B.

The analytical cost calculations of the auxiliary materials used in both Design Layouts are illustrated in the following Table:

Table 4-13: Analytical cost of the auxiliary materials



Auxiliary material		Unit price	Design Layout A		Design Layout B	
			Auxiliaries Demand	Auxiliaries Cost	Auxiliaries Demand	Auxiliaries Cost
for Production	Catalyst	4500 €/t	40,1 t/y	180514 €/y	40,1 t/y	180514 €/y
	Solid Heat Carrier	63 €/t	359,1 t/y	22506 €/y	-	-
	Air	0 €/m^3	2304000 m^3/y	0 €/y	2304000 m^3/y	0 €/y
	Cooling water	0,03 €/m^3	403200 m^3/y	12096 €/y	864000 m^3/y	25920 €/y
	Gas nitrogen	0,5 €/m^3	576 m^3/y	288 €/y	576 m^3/y	288 €/y
	Silica gel	0,2 €/kg	16200 kg/y	3240 €/y	16200 kg/y	3240 €/y
for Repair and Maintenance*		0,02 Equip.	-	19177 €/y	-	34145 €/y
for Laboratory*		0,005 I	-	16540 €/y	-	29450 €/y
*: Lipowatz-Kremezi, 2003			*Auxiliary Material Cost:*	254361 €/y	*Auxiliary Material Cost:*	273557 €/y

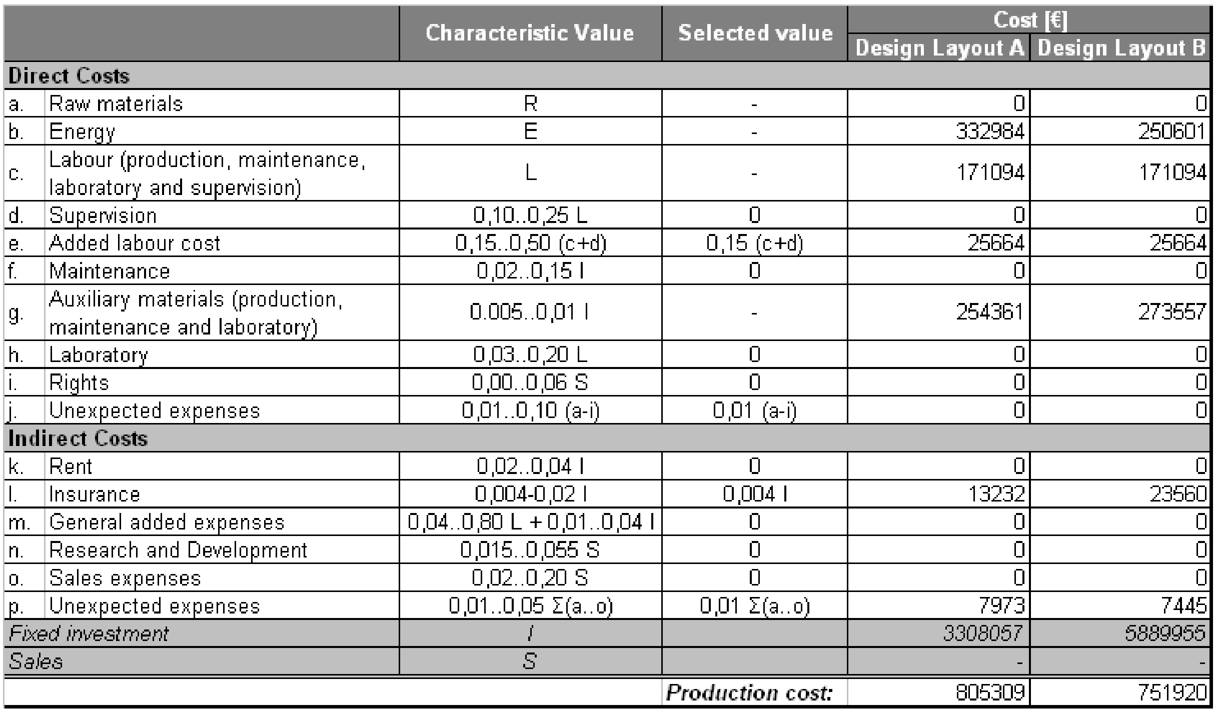
The cost of the catalytic material was the same for both Design Layouts. The increased demand for cooling water in induction heating systems was responsible for the higher cooling water cost for the Design Layout B. Because the equipment purchasing cost and the fixed investment cost for the Design Layout B were higher, the repair/maintenance and laboratory cost was increased. As a consequence, the total cost of the auxiliary materials was higher for the Design Layout B.

The unit price of the catalyst is a key factor for the feasibility of the KNV pilot plant. The cost of the synthetic zeolite can reach the price of 45000 €/t. For the present calculations, the unit price of the catalyst was 4500 €/t. Such a decrease in the price could be achieved by changing supplier or by changing the catalytic material. The use of a natural catalyst or a non-patented synthetic one with a lower production cost could be a possible alternative.

4.3.2.3 PRODUCTION COST

The following Table lists the basic factors of the production cost and their coefficients for the KNV pilot plant (Lipowatz-Kremezi, 2003):

Table 4-14: Basic factors of the production cost and their coefficients (Lipowatz-Kremezi, 2003)



		Characteristic Value	Selected value	Cost [€]	
				Design Layout A	Design Layout B
Direct Costs					
a.	Raw materials	R	-	0	0
b.	Energy	E	-	332984	250601
c.	Labour (production, maintenance, laboratory and supervision)	L	-	171094	171094
d.	Supervision	0,10..0,25 L	0	0	0
e.	Added labour cost	0,15..0,50 (c+d)	0,15 (c+d)	25664	25664
f.	Maintenance	0,02..0,15 I	0	0	0
g.	Auxiliary materials (production, maintenance and laboratory)	0.005..0,01 I	-	254361	273557
h.	Laboratory	0,03..0,20 L	0	0	0
i.	Rights	0,00..0,06 S	0	0	0
j.	Unexpected expenses	0,01..0,10 (a-i)	0,01 (a-i)	0	0
Indirect Costs					
k.	Rent	0,02..0,04 I	0	0	0
l.	Insurance	0,004-0,02 I	0,004 I	13232	23560
m.	General added expenses	0,04..0,80 L + 0,01..0,04 I	0	0	0
n.	Research and Development	0,015..0,055 S	0	0	0
o.	Sales expenses	0,02..0,20 S	0	0	0
p.	Unexpected expenses	0,01..0,05 Σ(a..o)	0,01 Σ(a..o)	7973	7445
Fixed investment		*I*		*3308057*	*5889955*
Sales		*S*		-	-
			Production cost:	805309	751920

The cost of supervision, maintanace and laboratory was already calculated in the labour cost. The cost of auxiliary materials was not calculated according to this model, but separately for reasons of accuracy. For the present calculations, it was assumed that there were no rights expenses, no rent expenses, no general expenses, no research and development expenses, no sales expenses and low uncertainty level for unexpected expenses.

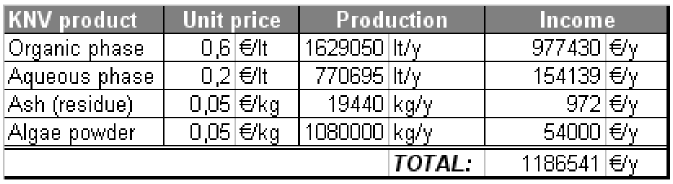
In the present calculations, the production cost was significantly affected by the energy costs. The production cost for the Design Layout A was higher than that for the Design Layout B.

4.4 ECONOMIC EVALUATION

For the economic evaluation of the two investment plans (Design Layout A and Design Layout B) the cash flows and the return of the investment periods (payback times) were calculated. The investment plan with the shorter payback time would be selected as the most beneficial one.

The KNV pilot plant would be making profit by selling: (a) the organic phase as biofuel to refineries for further post-treatment, (b) the aqueous phase as raw material to biochemical industries, (c) the ash produced by the residue regeneration as inorganic material (filler) to cement industries and (d) the algae powder produced by the size reduction processes as material for further use (e.g. animal feed). The sale price (in contrast to retail price) for these materials are presented at the Table below:

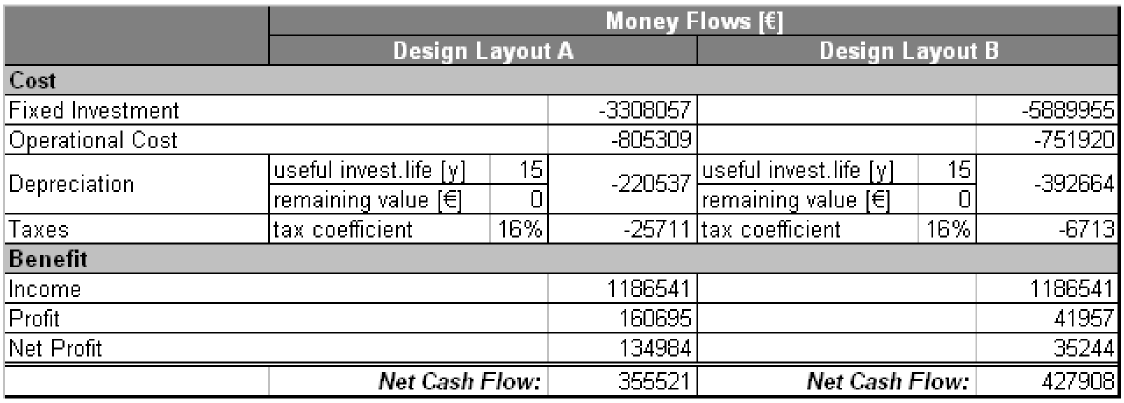
Table 4-15: Sale price of the KNV products



KNV product	Unit price		Production		Income	
Organic phase	0,6	€/lt	1629050	lt/y	977430	€/y
Aqueous phase	0,2	€/lt	770695	lt/y	154139	€/y
Ash (residue)	0,05	€/kg	19440	kg/y	972	€/y
Algae powder	0,05	€/kg	1080000	kg/y	54000	€/y
				TOTAL:	1186541	€/y

The money flows and the net cash flows for both Design Layouts are presented in the following Table:

Table 4-16: Money flows and net cash flows for the Design Layout A and B

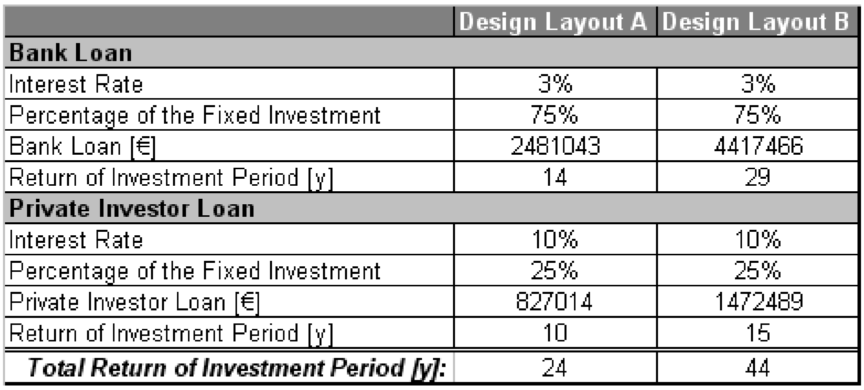


	Money Flows [€]					
	Design Layout A			Design Layout B		
Cost						
Fixed Investment			-3308057			-5889955
Operational Cost			-805309			-751920
Depreciation	useful invest.life [y]	15	-220537	useful invest.life [y]	15	-392664
	remaining value [€]	0		remaining value [€]	0	
Taxes	tax coefficient	16%	-25711	tax coefficient	16%	-6713
Benefit						
Income			1186541			1186541
Profit			160695			41957
Net Profit			134984			35244
	Net Cash Flow:		355521	***Net Cash Flow:***		427908

It was assumed that 75% of the fixed investment would be funded by the government in the form of loan with favourable terms (rate of return: 3%) to promote the penetration of biofuels into the Austrian market. The rest 25% of the fixed investment would be funded by private investors (rate of return: 10%).

It was assumed that the private investor would require 10 y of payback time for the Design Layout A and 15 y of payback time for the Design Layout B. The payback time for the bank loan and the total payback time for the whole investment are displayed in the Table below:

Table 4-17: Total return of investment periods for the Design Layouts A and B



	Design Layout A	Design Layout B
Bank Loan		
Interest Rate	3%	3%
Percentage of the Fixed Investment	75%	75%
Bank Loan [€]	2481043	4417466
Return of Investment Period [y]	14	29
Private Investor Loan		
Interest Rate	10%	10%
Percentage of the Fixed Investment	25%	25%
Private Investor Loan [€]	827014	1472489
Return of Investment Period [y]	10	15
Total Return of Investment Period [y]:	24	44

The payback time of the bank loan for the Design Layout A (24 y) was significantly lower than that of the Design Layout B (44 y). The increased purchasing cost of the induction heating systems resulted in a higher fixed investment cost. The operational cost was lower, but not low enough to prove the Design Layout B more profitable. A change in the energy prices (electricity, natural gas) could significantly affect the results. Both Design Layouts were expected to have the same product yields. The present calculations, based on the specific selected parameters, demonstrated that the Design Layout A was more profitable.

The biofuel prices are subject to variation, according to the biofuel demand and the conventional petroleum prices. If these factors increase, then the biofuel prices will also raise and the investment plans will appear more profitable. Biofuel industries require the support of funding and other actions on national or EU level to penetrate into the fuel market.

5 CONCLUSIONS

The low pressure catalytic co-conversion of safflower oil and rapeseed cake seems to be an interesting thermochemical process for the manufacture of transportation fuels and biochemicals. The catalyst addition to the biomass conversion system reduced the liquid phase yield and significantly changed its composition. The product mixture properties and composition depended on the process temperature and the catalyst used.

The liquid phase yields at 350 ℃ were low, while the main product was solid residue. Thus, this temperature is not recommended for biomass conversion. However, increasing the temperature to 400 ℃ significantly reduced coking and resulted in higher organic liquid phase yield.

The liquid phase characteristics varied by the use of different catalysts. The Fe-ZSM-5 zeolite did not show high cracking and deoxygenating ability. In its presence, a very low amount of lower hydrocarbons (C7-C15) formed. The organic liquid phase obtained on this catalyst was rich in oxygen and had a lower HHV.

The H-ZSM-5 zeolite possesses a better cracking activity, producing an organic liquid phase with a significantly lower oxygen content. However, the catalytic properties of this zeolite were restricted by the shape-selectivity effect, preventing the access of big molecules to its active sites. As a result, a significant part of the fatty acids remained unreacted.

The best results were gained on the H-Beta zeolite that possesses sufficiently strong acidic sites at absence of steric hindrances. Thus, the degree of biomass polymer and fatty acid conversion was the highest on this catalyst. The organic liquid product revealed lower oxygenated compound content and, respectively, the highest HHV. Comparing the results obtained on all catalysts, it was concluded that the H-Beta zeolite can be recommended to be applied in the co-conversion of vegetable oil and solid biomass to biofuel. The gained organic products were similar to fossil fuels by some important characteristics (HHV, density, viscosity), while other characteristics were even improved (such as sulfur content). Compared with other biofuels, i.e. pyrolysis oil or liquefaction oil, the gained organic products showed improved characteristics (HHV, density, viscosity, pH).

The produced aqueous phase contained chemical compounds, such as O- and Nheterocyclic compounds, that can be a valuable source of biochemicals.

The characteristics of the biofuel produced by the low pressure, catalytic conversion of rapeseed cake depended on the catalyst type and the presence of the vapour upgrading section. The addition of catalysts in the conversion system reduced the liquid phase yield compared with the non-catalytic test.

The organic liquid phases gained at the rapeseed cake conversion on H-ZSM-5 zeolite had a better quality than those produced when H-Beta zeolite was used. They had lower oxygen contents and higher HHV. The H-ZSM-5 zeolite possessed higher activity in cracking, producing a higher amount of aliphatic and aromatic hydrocarbons. The presence of the vapour upgrading section with this catalyst did not affect significantly the chemical composition; however, it resulted in an increased organic liquid phase yield. Thus, the use of the vapour upgrading section in the reactor with H-ZSM-5 zeolite favored an increased production of biofuel, which could be used in different liquid fuel applications.

The produced aqueous phase contained chemical compounds, such as O- and N-heterocyclic compounds, that can be a valuable source of biochemicals.

The biofuel characteristics of the low pressure, catalytic conversion of meat meal C1, with H-ZSM-5 zeolite at the absence of the vapour upgrading section, were different than those of the rapeseed cake conversion using the same parameters. The increased meat meal C1 ash content had as a result the residue increase. The organic phase consisted of increased amounts of valuable biofuel components, such as aliphatic and aromatic hydrocarbons. Still, the organic phase of the rapeseed cake conversion had a better quality, demonstrating a higher HHV and a lower water content.

The low pressure, catalytic conversion of algae, with H-ZSM-5 zeolite in the presence of the vapour upgrading section, resulted in a significantly increased biofuel yield compared with that of the rapeseed cake conversion test. The organic phase consisted of an increased amount of hydrocarbons (aliphatic and aromatic) and had a higher HHV than that of rapeseed cake as well as a density similar to diesel. Thus, the organic phase of the algae conversion had a better quality than the organic phase of the rapeseed cake conversion.

The produced aqueous phases of both meat meal C1 and algae conversion tests contained chemical compounds (e.g. N-heterocyclic compounds) that can be a valuable source of biochemicals.

The energy efficiency of the selected KNV laboratory tests, using H-ZSM-5 zeolite, increased by the following order: [meat meal C1 conversion] < [algae conversion] < [rapeseed cake conversion with vapour upgrading section] < [rapeseed cake conversion without vapour upgrading section] < [safflower oil and rapeseed cake co-conversion].

The increased products energy content of the co-conversion test resulted in a rise in its energy efficiency. On the contrary, the energy efficiency of the meat meal conversion was low. The increased energy content of the produced gas from the rapeseed cake conversion, in the absence of the vapour upgrading section, was responsible for the increased energy efficiency of this test, compared with that when the vapour upgrading section was present. Feedstocks with a significant humidity amount (e.g. algae) show an increased thermal energy demand for drying. As a result, the energy efficiency of their conversion is significantly lower compared with other tests.

The present feasibility studies calculations, based on the selected parameters, proved Design Layout A (with a conventional gas burner) more profitable than Design Layout B (with an induction heating system).

The technology selection significantly affected the fixed investment costs, while it had a negligible effect on the labour costs. The production costs depended on the used energy/fuel and its present unit prices. Any changes in these prices could significantly affect the production costs. The high catalyst price was also a key factor. The investment plan could only be profitable when a lower unit price and efficient catalyst regeneration was ensured. An increase in the conventional petroleum price could result in an increase in the produced biofuel price. That could make the investment plan for the erection of the KNV pilot plant more profitable. Still, biofuel industries need strategic and funding support on a national or EU level. In this way, the biofuel penetration into the fuel market will be possible.

6 ISSUES FOR FURTHER RESEARCH

Based on the results of the present work, the following issues for further research are suggested:

- the performance of laboratory tests using higher temperature (> 400 °C) and higher vacuum (< 0.9 bar), in order to explore their effect on the KNV conversion of different feedstocks

- the performance of algae conversion tests with the H-Beta catalyst in the presence and absence of the vapour upgrading section, in order to clarify the catalytic effect on the products

- the performance of meat meal C1 conversion tests with H-ZSM-5 in the presence of the vapour upgrading section and with H-Beta catalyst in the presence and absence of the vapour upgrading section, in order to clarify the catalytic effect on the products

- the application of different separation technologies for the removal of compounds from the organic phases, which should not be present in biofuels

- the application of different separation technologies for isolating valuable compounds of the aqueous phases

- the performance of a market study for the utilization of the aqueous phases as a source of biochemicals

- the performance of laboratory tests with other promising catalytic materials (natural or synthetic ones) for the KNV conversion of biogenic feedstocks into biofuels

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8 ANNEX

8.1 BIOMASS DATABASE

Table 8-1: Biomass database

			untreated wood											treated wood
OVERVIEW			AVERAGE	beech	pine	fir	pine	oak	hybrid poplar	poplar	eucalyptus	black locust	willow	AVERAGE
water content		wt% wet	18,8	-	-	-	4	-	6,9	-	9,3	-	1,2	14,3
volatiles		wt% daf	81,9	-	84,8	-	-	-	87,2	-	87,1	81,6	81,7	80,3
ash		wt% dry	2,2	0,6	0,1	-	0,1	-	2,7	0,6	0,5	0,8	1,3	5
HHV		kJ/kg daf	20125	18921	20243	20173^1	20243	19078^1	19550	20886	19320	19869	19352	20165
LHVcalc		kJ/kg daf	18779	17695	18897	18820^1	18897	17769^1	18191	19511	18059	18613	18091	18809
ultimate analysis	C	wt% daf	50,7	49	52	49,6^1	52	49,5^1	51,6	52	49,8	51,1	45,3	51,3
	H	wt% daf	6,06	5,8	6,2	6,2^1	6,2	6^1	6,2	6,3	5,8	5,8	5,8	6,04
	O	wt% daf	42,8	45	41,7	44,2^1	41,7	44,5^1	41,6	41,7	44,2	42,3	46,8	41,4
	N	wt% daf	0,37	0,12	0,12	-	0,12	-	0,62	-	0,14	0,57	0,2	1,24
	S	wt% daf	0,07	-	0,03	-	0,03	-	0,02	-	0,03	0,01	0,03	0,1
	Cl	wt% daf	0,054	-	0,02	-	0,02	-	0,01	-	0,055	0,081	0,01	0,088
	F	wt% daf	0,004	-	-	-	-	-	-	-	-	-	0,001	0,003
	Br	wt% daf	-	-	-	-	-	-	-	-	-	-	-	-
biomass analysis	Al	mg/kg dry	369	-	-	-	-	-	-	-	-	-	18,9	1670,5
	As	mg/kg dry	1,2	-	-	-	-	-	-	-	-	-	0,7	252,8
	B	mg/kg dry	9,5	-	-	-	-	-	-	-	-	-	5,8	12,7
	Ba	mg/kg dry	120,5	-	-	-	-	-	-	-	-	-	1,2	188,2
	Ca	mg/kg dry	11199,7	-	-	-	-	-	-	-	-	-	3899	5104,9
	Cd	mg/kg dry	0,6	-	-	-	-	-	-	-	-	-	1,9	0,9
	Co	mg/kg dry	2,4	-	-	-	-	-	-	-	-	-	0	4,1
	Cr	mg/kg dry	18,8	-	-	-	-	-	-	-	-	-	2,1	274,1
	Cu	mg/kg dry	20,9	-	-	-	-	-	-	-	-	-	3,1	122,7
	Fe	mg/kg dry	266	-	-	-	-	-	-	-	-	-	30	1394
	Hg	mg/kg dry	0,1	-	-	-	-	-	-	-	-	-	-	0,3
	K	mg/kg dry	1851,5	-	-	-	-	-	-	-	-	-	1420	1747,6
	Mg	mg/kg dry	760,6	-	-	-	-	-	-	-	-	-	378	614,3
	Mn	mg/kg dry	171,3	-	-	-	-	-	-	-	-	-	12	98,3
	Mo	mg/kg dry	4	-	-	-	-	-	-	-	-	-	0,2	1
	Na	mg/kg dry	360,8	-	-	-	-	-	-	-	-	-	127,2	966,7
	Ni	mg/kg dry	23,9	-	-	-	-	-	-	-	-	-	11,2	48,7
	P	mg/kg dry	450,4	-	-	-	-	-	-	-	-	-	651,6	398,1
	Pb	mg/kg dry	26,3	-	-	-	-	-	-	-	-	-	1,9	246,4
	Sb	mg/kg dry	2,1	-	-	-	-	-	-	-	-	-	2,9	3,3
	Se	mg/kg dry	2,8	-	-	-	-	-	-	-	-	-	20,6	0,7
	Si	mg/kg dry	2367,2	-	-	-	-	-	-	-	-	-	69,1	14458,1
	Sn	mg/kg dry	1,4	-	-	-	-	-	-	-	-	-	0,2	1,5
	Sr	mg/kg dry	15,5	-	-	-	-	-	-	-	-	-	14,4	27,4
	Te	mg/kg dry	3,5	-	-	-	-	-	-	-	-	-	-	2,4
	Ti	mg/kg dry	31,2	-	-	-	-	-	-	-	-	-	2,1	218,4
	V	mg/kg dry	3,5	-	-	-	-	-	-	-	-	-	0,2	3,2
	Zn	mg/kg dry	52,5	-	-	-	-	-	-	-	-	-	61,8	374,4

			untreated wood											treated wood
OVERVIEW			AVERAGE	beech	pine	fir	pine	oak	hybrid poplar	poplar	eucalyptus	black locust	willow	AVERAGE
biochemical composition	Cellulose	wt.% dry	39,8	-	-	-	44,55	-	44,7	-	49,5	41,61	-	40,9
	Hemicellulose	wt.% dry	23,3	-	-	-	21,9	-	18,55	-	13,07	17,66	-	14,2
	Lignine	wt.% dry	24,8	-	-	-	27,67	-	26,44	-	27,71	26,79	-	24,6
	Lignin acid insoluble (AIL)	wt.% dry	25	-	-	-	-	-	-	-	-	-	-	23
	Lignin acid soluble (ASL)	wt.% dry	2	-	-	-	-	-	-	-	-	-	-	0
	Lipids	wt.% dry	8,2	-	-	-	-	-	-	-	-	-	-	-
	Proteine	wt.% dry	4,9	-	-	-	-	-	-	-	-	-	-	-
	Extractives EtOH/toluene	wt.% dry	2,5	-	-	-	2,98	-	7,12	-	4,27	7,31	-	2,9
	Extractives 95% EtOH	wt.% dry	1,5	-	-	-		-		-			-	1,2
	Extractives hot water	wt.% dry	6,4	-	-	-		-		-			-	9,4
	Starch	wt.% dry	1,7	-	-	-	-	-	-	-	-	-	-	-
	Pectin	wt.% dry	5,3	-	-	-	-	-	-	-	-	-	-	2,6
	Arabinan C5	wt.% dry	0,9	0	0	0	1,6	0	0,82	0	0,31	0,94	0	0,5
	Xylan C5	wt.% dry	13,2	0	0	0	6,3	0	14,56	0	10,73	13,86	0	9
	Mannan C6	wt.% dry	4,1	0	0	0	11,43	0	2,2	0	1,27	1,92	0	5,5
	Galactan C6	wt.% dry	1,5	0	0	0	2,56	0	0,97	0	0,76	0,93	0	0,9
	Glucan C6	wt.% dry	42,7	0	0	0	44,55	0	44,7	0	49,5	41,61	0	40,2
	Rhamnan C6	wt.% dry	0,3	0	0	0	-	0	-	0	-	-	0	0,1
	Total non-structural carbohydrates (TNC)	wt.% dry	26,5	-	-	-	-	-	-	0	-	-	0	-

			grass/plant							**straw (stalks, cobs, ears)**						
OVERVIEW			AVERAGE	alfalfa (lucern)	alfalfa	clover grass	hemp	miscanthus	switch grass	AVERAGE	barley	maize / corn	rape	rice	sunflower	wheat
water content		wt% wet	30,1	10	-		-	40	-	15,4	-	-	-	-	-	9,7
volatiles		wt% daf	82,6	81,6	-		-		-	81,1	-	-	-	-	-	-
ash		wt% dry	6,9	9,4	10,3	3,5	6,9	4,8	10,1	7,4	4,9	8,5	5,5	19,1	3,5	5,9
HHV		kJ/kg daf	19590	20530	20231	19640	18889	20021	20051	19346	19739	19333	22871	19718	26892	19928
LHVcalc		kJ/kg daf	18288	19085	19012		17668	18751	18653	18007	18460	18043	21371	18440	25237	18606
ultimate analysis	C	wt% daf	49,2	49,7	50,3	46,5	48,1	50,3	53,2	48,6	49,2	48,8	54,1	48,1	62,5	47,6
	H	wt% daf	5,95	6,6	5,5	7	5,6	5,8	6,4	5,96	5,8	5,9	6,8	5,9	7,4	6,1
	O	wt% daf	43,5	40,7	39,7	43,7	45	43	39	43,2	44,1	43,2	36	43,6	27,8	45,3
	N	wt% daf	1,21	2,76	3,68	2,28	1,06	0,57	1,3	0,91	0,43	0,45	2,43	1,69	2,07	0,85
	S	wt% daf	0,17	2,21	0,18	0,31	0,08	0,12	0,11	0,15	0,06	0,05	0,42	0,14	0,12	0,1
	Cl	wt% daf	0,351	0,331	0,658	0,124	0,172	0,189	-	0,53	0,431	1,617	0,275	0,581	0,114	0,234
	F	wt% daf	0,002	-	-	-	-	-	-	0,002	-	-	-	-	-	-
	Br	wt% daf		-	-	-	-	-	-	-	-	-	-	-	-	-
biomass analysis	Al	mg/kg dry	239,3	-	-	-	-	-	-	3021,4	-	-	-	-	-	-
	As	mg/kg dry	0,6	-	-	-	-	-	-	1,3	-	-	-	-	-	-
	B	mg/kg dry	13,4	-	-	-	-	-	-	15,8	-	-	-	-	-	-
	Ba	mg/kg dry	6,4	-	-	-	-	-	-	64,8	-	-	-	-	-	-
	Ca	mg/kg dry	6744,6	-	-	6400Msr	-	-	-	4755,6	-	-	-	-	-	-
	Cd	mg/kg dry	0,3	-	0,1	-	0,4	0,1	-	0,1	0,1	0,1	0,1	-	0,2	-
	Co	mg/kg dry	0,6	-	-	-	-	-	-	1,6	-	-	-	-	-	-
	Cr	mg/kg dry	2,1	-	-	-	-	-	-	23,9	-	-	-	-	-	-
	Cu	mg/kg dry	6,1	-	5,9	-	3,9	2,2	-	5,5	2,6	3,7	2,5	-	19,4	-
	Fe	mg/kg dry	224,5	-	-	1500 Msr	-	-	-	1170,5	-	-	-	-	-	-
	Hg	mg/kg dry	0,1	-	0	-	0	0	-	0	0	-	-	-	-	-
	K	mg/kg dry	11292,1	-	-	11000 Msr	-	-	-	11635,3	-	-	-	-	-	-
	Mg	mg/kg dry	1052,5	-	-	-	-	-	-	1847,9	-	-	-	-	-	-
	Mn	mg/kg dry	38,7	-	-	-	-	-	-	94,9	-	-	-	-	-	-
	Mo	mg/kg dry	5,6	-	-	-	-	-	-	1,1	-	-	-	-	-	-
	Na	mg/kg dry	691,7	-	-	-	-	-	-	1046	-	-	-	-	-	-
	Ni	mg/kg dry	1,7	-	-	-	-	-	-	92,1	-	-	-	-	-	-
	P	mg/kg dry	1704,5	-	-	3200 Msr	-	-	-	1037,8	-	-	-	-	-	-
	Pb	mg/kg dry	2,2	-	2,9	-	0,3	2,3	-	2,1	2,8	3,7	0,4	-	0,3	-
	Sb	mg/kg dry	1,1	-	-	-	-	-	-	2,9	-	-	-	-	-	-
	Se	mg/kg dry	0,9	-	-	-	-	-	-	0,7	-	-	-	-	-	-
	Si	mg/kg dry	9383,6	-	-	1700 Msr	-	-	-	14612,1	-	-	-	-	-	-
	Sn	mg/kg dry	1,7	-	-	-	-	-	-	0,9	-	-	-	-	-	-
	Sr	mg/kg dry	28,9	-	-	-	-	-	-	59	-	-	-	-	-	-
	Te	mg/kg dry	1	-	-	-	-	-	-	-	-	-	-	-	-	-
	Ti	mg/kg dry	11,2	-	-	-	-	-	-	105,1	-	-	-	-	-	-
	V	mg/kg dry	0,8	-	-	-	-	-	-	3,8	-	-	-	-	-	-
	Zn	mg/kg dry	55,6	-	-	-	-	-	-	20,6	-	-	-	-	-	-

			grass/plant							straw (stalks, cobs, ears)						
OVERVIEW			AVERAGE	alfalfa (lucern)	alfalfa	clover grass	hemp	miscanthus	switch grass	AVERAGE	barley	maize / corn	rape	rice	sunflower	wheat
biochemical composition	Cellulose	wt.% dry	43,9	-	-	-	-	-	31,98	36	-	-	-	-	-	-
	Hemicellulose	wt.% dry	19,7	-	-	-	-	-	25,19	24	-	-	-	-	-	-
	Lignine	wt.% dry	10,9	-	-	-	-	-	18,13	13,5	-	-	-	-	-	-
	Lignin acid insoluble (AIL)	wt.% dry	12	-	-	-	-	-	-	16	-	-	-	-	-	-
	Lignin acid soluble (ASL)	wt.% dry	1	-	-	-	-	-	-	-	-	-	-	-	-	-
	Lipids	wt.% dry	14	-	-	-	-	-	-	4,4	-	-	-	-	-	-
	Proteine	wt.% dry	13	-	-	-	-	-	-	4,8	-	-	-	-	-	-
	Extractives EtOH/toluene	wt.% dry	4,6	-	-	-	-	-	17,54	5,4	-	-	-	-	-	-
	Extractives 95% EtOH	wt.% dry	1,1	-	-	-	-	-		-	-	-	-	-	-	-
	Extractives hot water	wt.% dry	5,1	-	-	-	-	-		6,2	-	-	-	-	-	-
	Starch	wt.% dry	0	-	-	-	-	-	-	71,5	-	-	-	-	-	-
	Pectin	wt.% dry	3,3	-	-	-	-	-	-	-	-	-	-	-	-	-
	Arabinan C5	wt.% dry	1,3	0	0	0	0	0	2,84	3,1	0	0	0	0	0	0
	Xylan C5	wt.% dry	12	0	0	0	0	0	21,09	19	0	0	0	0	0	0
	Mannan C6	wt.% dry	1,4	0	0	0	0	0	0,3	0,6	0	0	0	0	0	0
	Galactan C6	wt.% dry	1,3	0	0	0	0	0	0,95	1	0	0	0	0	0	0
	Glucan C6	wt.% dry	48	0	0	0	0	0	31,98	35,7	0	0	0	0	0	0
	Rhamnan C6	wt.% dry	0,3	0	0	0	0	0	0	-	0	0	0	0	0	0
	Total non-structural carbohydrates (TNC)	wt.% dry	9,7	-	-	-	0	0	0	0,9	-	-	-	-	-	-

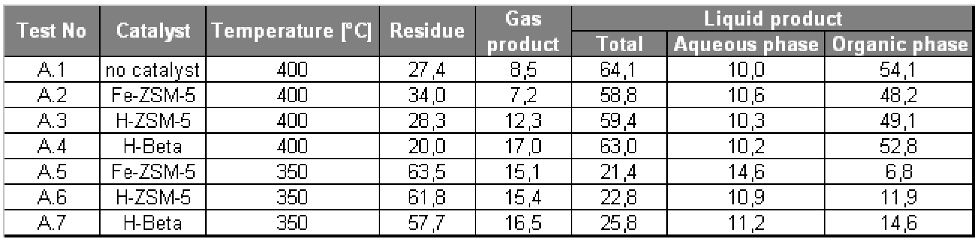
			husk/shell/peat				**organic residue/product**									**algae**	**manure**	**sludge**
OVERVIEW			AVERAGE	rice (hull)	sunflower (shell)	walnuts (hull)	AVERAGE	draff ("Treber") from Göss	draff ("Treber") from Puntigam	draff ("Treber") from Schwechat	draff ("Treber") from Wieselburg	draff ("Treber") from Zipf	bone and meat meal	bone meal	bagasse	AVERAGE	AVERAGE	AVERAGE
water content		wt% wet	10	4	-	47,8	27	78,7	78,2	-	78,7	79,2	1,9	5	55	31,9	43,1	32
volatiles		wt% daf	76,7	79,9	79,4	82	84,6	-	-	-	-	-	90,4	-	87,5	85,2	80,4	87,7
ash		wt% dry	5,7	17,4	4	3	10,5	4,33	4,77	-	-	-	18,8	15	3,8	6,1	28,5	34,8
HHV		kJ/kg daf	20424	19824	18750	22867	21030	-	-	-	-	-	26116	21176	18950	24754	20251	21091
LHVcalc		kJ/kg daf	19055	18465	17432	21401	19089	-	-	-	-	-	24315	-	17663	23147	18845	19782
ultimate analysis	C	wt% daf	50,2	50,1	49,4	55,1	49,7	47,1	46,8	-	-	-	56,9	-	47,7	53,8	46,4	50,3
	H	wt% daf	6,16	6,2	6	6,7	6,52	6,76	6,71	-	-	-	8,3	-	5,9	7,37	6,44	7,17
	O	wt% daf	42,6	43	43,1	36,4	41,6	-	-	-	-	-	21	-	44,6	30,9	36,1	35,1
	N	wt% daf	1,12	0,62	1,46	1,58	2,34	3,8	3,4	-	-	-	11,95	11,06	1,8	7,52	5,3	5,32
	S	wt% daf	0,16	0,1	0,05	0,11	0,67	2580	2200	-	-	-	0,8	0,24	-	0,48	0,76	1,78
	Cl	wt% daf	0,086	-	-	0,021	0,318	2107	1807	-	-	-	1,084	1,059	-	0,12	1,031	0,287
	F	wt% daf	0,001	-	-	-	0,005	<20^{2}	<20^{2}	-	-	-	-	-	-	-	-	0,028
	Br	wt% daf	-	-	-	-	0,02	-	-	-	-	-	-	-	-	-	-	-
biomass analysis	Al	mg/kg dry	1110	-	-	-	2678,6	41	21	17	40	31	200 Msr	-	-	-	844,7	21431,3
	As	mg/kg dry	4,8	-	-	-	1,6	<0,05	<0,05	<0,05	<0,05	<0,05	-	-	-	-	1,4	9,6
	B	mg/kg dry	19,3	-	-	-	-	-	-	-	-	-	-	-	-	-	32,7	112,4
	Ba	mg/kg dry	194,7	-	-	-	163,7	7,8	8,4	10	11,7	11,2	-	-	-	-	20,4	399,9
	Ca	mg/kg dry	4800	-	-	-	26677,5	2700	3570	3800	3100	3300	57000 Msr	45000 Msr	-	725	44007,6	75094,1
	Cd	mg/kg dry	0,7	-	-	-	2,6	0,032	0,027	0,04	0,04	0,044	-	-	-	-	0,4	3,7
	Co	mg/kg dry	2,3	-	-	-	4,3	0,026	0,024	0,021	0,035	0,029	-	2 Msr	-	-	1,1	11,3
	Cr	mg/kg dry	23,5	-	-	-	33,5	0,69	0,79	0,19	1,4	0,67	-	4 Msr	-	-	28,7	1812,6
	Cu	mg/kg dry	70,5	-	-	-	44,3	15	15	24	26	26	-	30 Msr	-	-	60,4	1034,3
	Fe	mg/kg dry	1010	-	-	-	4688,1	128	111	164	144	120	1270 Msr	1700 Msr	-	-	1137,5	23493,9
	Hg	mg/kg dry	0,2	-	-	-	0,4	<0,02	<0,02	<0,02	<0,02	<0,02	-	0	-	-	-	2
	K	mg/kg dry	15837,5	-	-	-	4778,3	245	64	650	330	450	6700 Msr	6000 Msr	-	6400	32337,1	3829
	Mg	mg/kg dry	3940	-	-	-	1841,8	2400	2030	2800	2400	2400	1700 Msr	1700 Msr	-	1390	6450,9	4065,3
	Mn	mg/kg dry	92,4	-	-	-	21,2	39	42	46	41	44	-	25 Msr	-	-	276	434,1
	Mo	mg/kg dry	2,9	-	-	-	18,3	1,52	1,79	1,65	1,4	1,5	-	-	-	-	3,8	8,2
	Na	mg/kg dry	539,8	-	-	-	49689,2	53	62	17	16	23	8200 Msr	10500 Msr	-	980	8475,1	2463,7
	Ni	mg/kg dry	14,1	-	-	-	14,9	0,45	0,52	0,25	0,64	0,48	-	3 Msr	-	-	17	384,4
	P	mg/kg dry	3640	-	-	-	13227,9	7200	7900	9100	7400	8000	29600 Msr	16500 Msr	-	2700	17586,9	15413,1
	Pb	mg/kg dry	219,7	-	-	-	55,1	0,11	0,096	0,083	0,15	0,25	-	2 Msr	-	-	13,8	248,6
	Sb	mg/kg dry	5,6	-	-	-	1,1	-	-	-	-	-	-	-	-	-	0,7	6,2
	Se	mg/kg dry	2	-	-	-	0,9	-	-	-	-	-	-	-	-	-	1,3	4,8
	Si	mg/kg dry	5710	-	-	-	7261,7	3500	4900	-	-	-	900 Msr	-	-	125	4426	43216,7
	Sn	mg/kg dry	4,1	-	-	-	5,8	-	-	-	-	-	-	-	-	-	0,7	34
	Sr	mg/kg dry	28,7	-	-	-	31	-	-	-	-	-	-	-	-	-	39,8	504,9
	Te	mg/kg dry	1,1	-	-	-	1	-	-	-	-	-	-	-	-	-	-	11,7
	Ti	mg/kg dry	187,8	-	-	-	29,5	41	49	10	48	42	19 Msr	-	-	-	46,2	1526,8
	V	mg/kg dry	3,6	-	-	-	1	0,1	0,047	0,036	0,083	0,072	-	-	-	-	2,9	22
	Zn	mg/kg dry	215,2	-	-	-	195,5	96	94	100	111	100	-	130 Msr	-	-	268,5	2258,5

			husk/shell/peat				**organic residue/product**									**algae**	**manure**	**sludge**
OVERVIEW			AVERAGE	rice (hull)	sunflower (shell)	walnuts (hull)	AVERAGE	draff ("Treber") from Göss	draff ("Treber") from Puntigam	draff ("Treber") from Schwechat	draff ("Treber") from Wieselburg	draff ("Treber") from Zipf	bone and meat meal	bone meal	bagasse	AVERAGE	AVERAGE	AVERAGE
biochemical composition	Cellulose	wt.% dry	27,6	69,9	48,4	-	36,5	-	-	-	-	-	-	-	-	30	23,1	35,8
	Hemicellulose	wt.% dry	20,2	24,3	34,6	-	18,8	-	-	-	-	-	-	-	-	35	26,7	17,1
	Lignine	wt.% dry	31,3	14,3	17	-	15,6	-	-	-	-	-	-	-	-	-	11,3	16,8
	Lignin acid insoluble (AIL)	wt.% dry	37	-	-	-	19	-	-	-	-	-	-	-	-	-	-	-
	Lignin acid soluble (ASL)	wt.% dry	1	-	-	-	0	-	-	-	-	-	-	-	-	-	-	-
	Lipids	wt.% dry	0,4	-	-	-	9,6	-	-	-	-	-	-	-	-	-	2,1	-
	Proteine	wt.% dry	3,2	-	-	-	17,9	-	-	-	-	-	-	-	-	46,8	24	5,5
	Extractives EtOH/toluene	wt.% dry	3,5	-	2,7	-	1,7	-	-	-	-	-	-	-	-	-	-	-
	Extractives 95% EtOH	wt.% dry	1,1	-	-	-	0,7	-	-	-	-	-	-	-	-	-	-	-
	Extractives hot water	wt.% dry	6,7	-	-	-	2,8	-	-	-	-	-	-	-	-	-	-	-
	Starch	wt.% dry	3	-	-	-	39	-	-	-	-	-	-	-	-	-	-	50
	Pectin	wt.% dry	4,8	-	-	-	2,6	-	-	-	-	-	-	-	-	-	-	15
	Arabinan C5	wt.% dry	1,5	0	0	0	0,9	-	-	-	-	-	0	0	0	-	-	13,2
	Xylan C5	wt.% dry	14,1	0	0	0	9,8	-	-	-	-	-	0	0	0	-	-	-
	Mannan C6	wt.% dry	0,3	0	0	0	6,1	-	-	-	-	-	0	0	0	-	-	-
	Galactan C6	wt.% dry	0,8	0	0	0	0,8	-	-	-	-	-	0	0	0	-	-	2,8
	Glucan C6	wt.% dry	27,6	0	0	0	50,2	-	-	-	-	-	0	0	0	-	-	-
	Rhamnan C6	wt.% dry	0,2	0	0	0	0,1	-	-	-	-	-	0	0	0	-	-	-
	Total non-structural carbohydrates (TNC)	wt.% dry	-	-	-	-	55,7	-	-	-	-	-	-	-	-	-	-	-

8.2 MASS BALANCES OF THE PERFORMED TESTS

8.2.1 CO-CONVERSION OF RAPESEED CAKE AND SAFFLOWER OIL

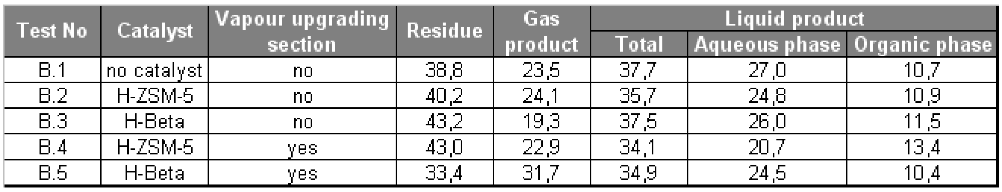
Table 8-2: Product yields (wt. % on biogenic mixture) of the performed rapeseed cake and safflower oil co-conversion tests



Test No	Catalyst	Temperature [°C]	Residue	Gas product	Liquid product		
					Total	Aqueous phase	Organic phase
A.1	no catalyst	400	27,4	8,5	64,1	10,0	54,1
A.2	Fe-ZSM-5	400	34,0	7,2	58,8	10,6	48,2
A.3	H-ZSM-5	400	28,3	12,3	59,4	10,3	49,1
A.4	H-Beta	400	20,0	17,0	63,0	10,2	52,8
A.5	Fe-ZSM-5	350	63,5	15,1	21,4	14,6	6,8
A.6	H-ZSM-5	350	61,8	15,4	22,8	10,9	11,9
A.7	H-Beta	350	57,7	16,5	25,8	11,2	14,6

8.2.2 RAPESEED CAKE CONVERSION WITH TWO REACTOR CONFIGURATIONS

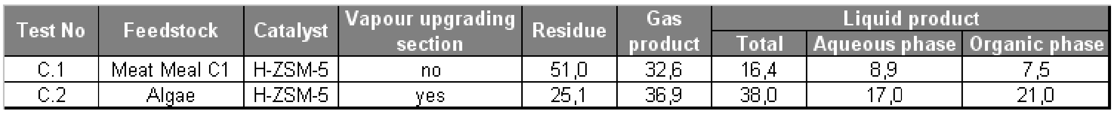
Table 8-3: Product yields (wt. % on biogenic mixture) of the performed rapeseed cake conversion tests using two reactor configurations



Test No	Catalyst	Vapour upgrading section	Residue	Gas product	Liquid product		
					Total	Aqueous phase	Organic phase
B.1	no catalyst	no	38,8	23,5	37,7	27,0	10,7
B.2	H-ZSM-5	no	40,2	24,1	35,7	24,8	10,9
B.3	H-Beta	no	43,2	19,3	37,5	26,0	11,5
B.4	H-ZSM-5	yes	43,0	22,9	34,1	20,7	13,4
B.5	H-Beta	yes	33,4	31,7	34,9	24,5	10,4

8.2.3 MEAT MEAL C1 AND ALGAE CONVERSION

Table 8-4: Product yields (wt. % on biogenic mixture) of the performed separate meat meal C1 and algae conversion tests

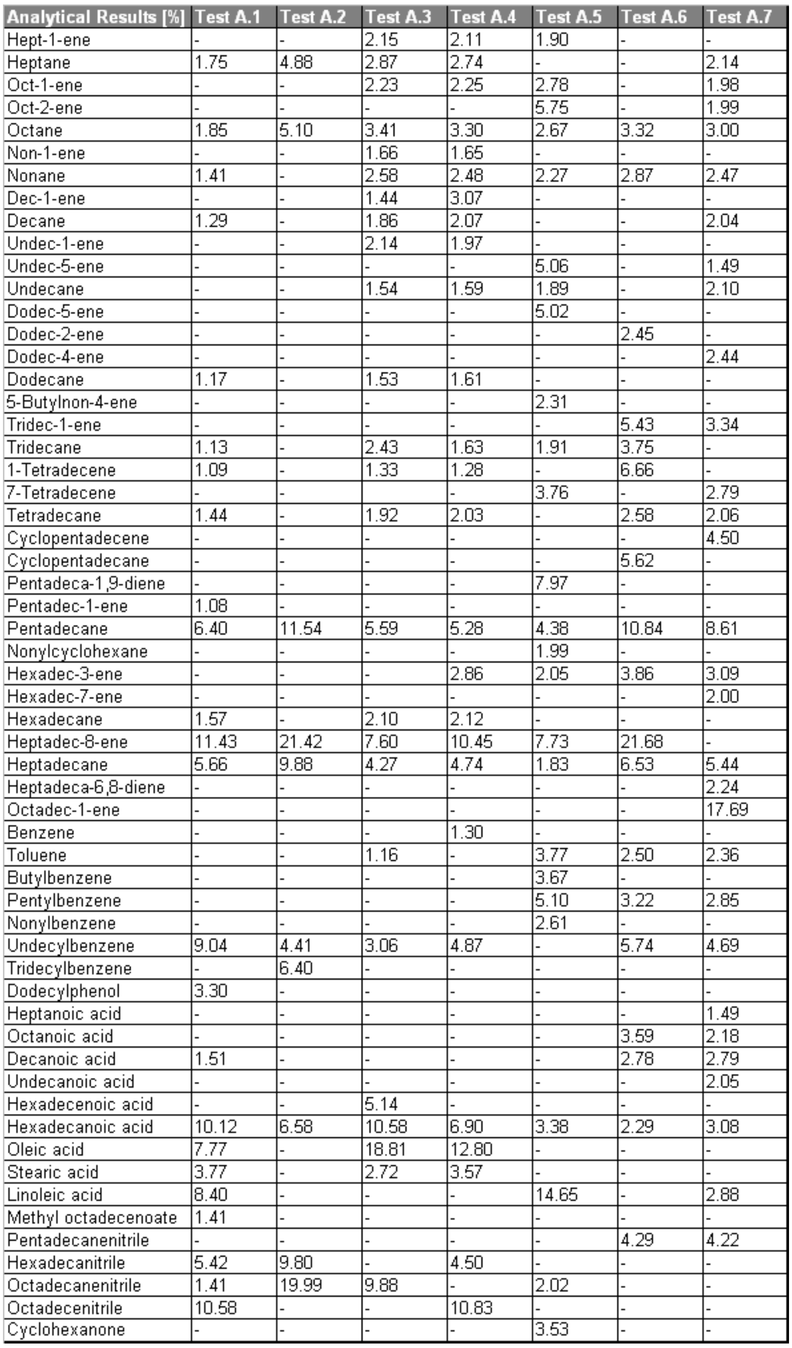


Test No	Feedstock	Catalyst	Vapour upgrading section	Residue	Gas product	Liquid product		
						Total	Aqueous phase	Organic phase
C.1	Meat Meal C1	H-ZSM-5	no	51,0	32,6	16,4	8,9	7,5
C.2	Algae	H-ZSM-5	yes	25,1	36,9	38,0	17,0	21,0

8.3 DETAILED COMPOSITION OF THE LIQUID PRODUCTS

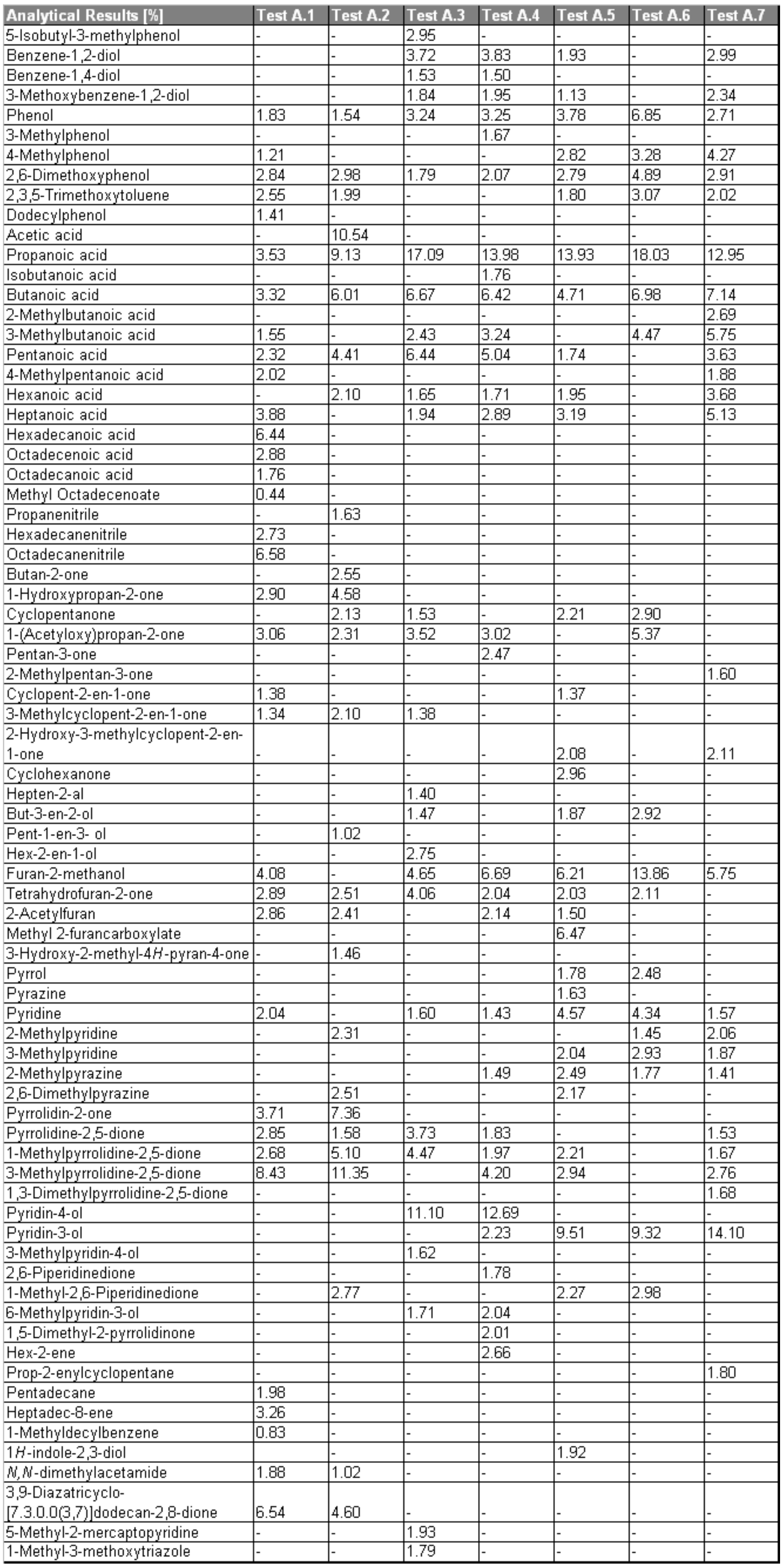
8.3.1 CO-CONVERSION OF RAPESEED CAKE AND SAFFLOWER OIL

Table 8-5: Organic phase detailed composition of the performed rapeseed cake and safflower oil co-conversion tests



Analytical Results [%]	Test A.1	Test A.2	Test A.3	Test A.4	Test A.5	Test A.6	Test A.7
Hept-1-ene	-	-	2.15	2.11	1.90	-	-
Heptane	1.75	4.88	2.87	2.74	-	-	2.14
Oct-1-ene	-	-	2.23	2.25	2.78	-	1.98
Oct-2-ene	-	-	-	-	5.75	-	1.99
Octane	1.85	5.10	3.41	3.30	2.67	3.32	3.00
Non-1-ene	-	-	1.66	1.65	-	-	-
Nonane	1.41	-	2.58	2.48	2.27	2.87	2.47
Dec-1-ene	-	-	1.44	3.07	-	-	-
Decane	1.29	-	1.86	2.07	-	-	2.04
Undec-1-ene	-	-	2.14	1.97	-	-	-
Undec-5-ene	-	-	-	-	5.06	-	1.49
Undecane	-	-	1.54	1.59	1.89	-	2.10
Dodec-5-ene	-	-	-	-	5.02	-	-
Dodec-2-ene	-	-	-	-	-	2.45	-
Dodec-4-ene	-	-	-	-	-	-	2.44
Dodecane	1.17	-	1.53	1.61	-	-	-
5-Butylnon-4-ene	-	-	-	-	2.31	-	-
Tridec-1-ene	-	-	-	-	-	5.43	3.34
Tridecane	1.13	-	2.43	1.63	1.91	3.75	-
1-Tetradecene	1.09	-	1.33	1.28	-	6.66	-
7-Tetradecene	-	-		-	3.76	-	2.79
Tetradecane	1.44	-	1.92	2.03	-	2.58	2.06
Cyclopentadecene	-	-	-	-	-	-	4.50
Cyclopentadecane	-	-	-	-	-	5.62	-
Pentadeca-1,9-diene	-	-	-	-	7.97	-	-
Pentadec-1-ene	1.08	-	-	-	-	-	-
Pentadecane	6.40	11.54	5.59	5.28	4.38	10.84	8.61
Nonylcyclohexane	-	-	-	-	1.99	-	-
Hexadec-3-ene	-	-	-	2.86	2.05	3.86	3.09
Hexadec-7-ene	-	-	-	-	-	-	2.00
Hexadecane	1.57	-	2.10	2.12	-	-	-
Heptadec-8-ene	11.43	21.42	7.60	10.45	7.73	21.68	-
Heptadecane	5.66	9.88	4.27	4.74	1.83	6.53	5.44
Heptadeca-6,8-diene	-	-	-	-	-	-	2.24
Octadec-1-ene	-	-	-	-	-	-	17.69
Benzene	-	-	-	1.30	-	-	-
Toluene	-	-	1.16	-	3.77	2.50	2.36
Butylbenzene	-	-	-	-	3.67	-	-
Pentylbenzene	-	-	-	-	5.10	3.22	2.85
Nonylbenzene	-	-	-	-	2.61	-	-
Undecylbenzene	9.04	4.41	3.06	4.87	-	5.74	4.69
Tridecylbenzene	-	6.40	-	-	-	-	-
Dodecylphenol	3.30	-	-	-	-	-	-
Heptanoic acid	-	-	-	-	-	-	1.49
Octanoic acid	-	-	-	-	-	3.59	2.18
Decanoic acid	1.51	-	-	-	-	2.78	2.79
Undecanoic acid	-	-	-	-	-	-	2.05
Hexadecenoic acid	-	-	5.14	-	-	-	-
Hexadecanoic acid	10.12	6.58	10.58	6.90	3.38	2.29	3.08
Oleic acid	7.77	-	18.81	12.80	-	-	-
Stearic acid	3.77	-	2.72	3.57	-	-	-
Linoleic acid	8.40	-	-	-	14.65	-	2.88
Methyl octadecenoate	1.41	-	-	-	-	-	-
Pentadecanenitrile	-	-	-	-	-	4.29	4.22
Hexadecanitrile	5.42	9.80	-	4.50	-	-	-
Octadecanenitrile	1.41	19.99	9.88	-	2.02	-	-
Octadecenitrile	10.58	-	-	10.83	-	-	-
Cyclohexanone	-	-	-	-	3.53	-	-

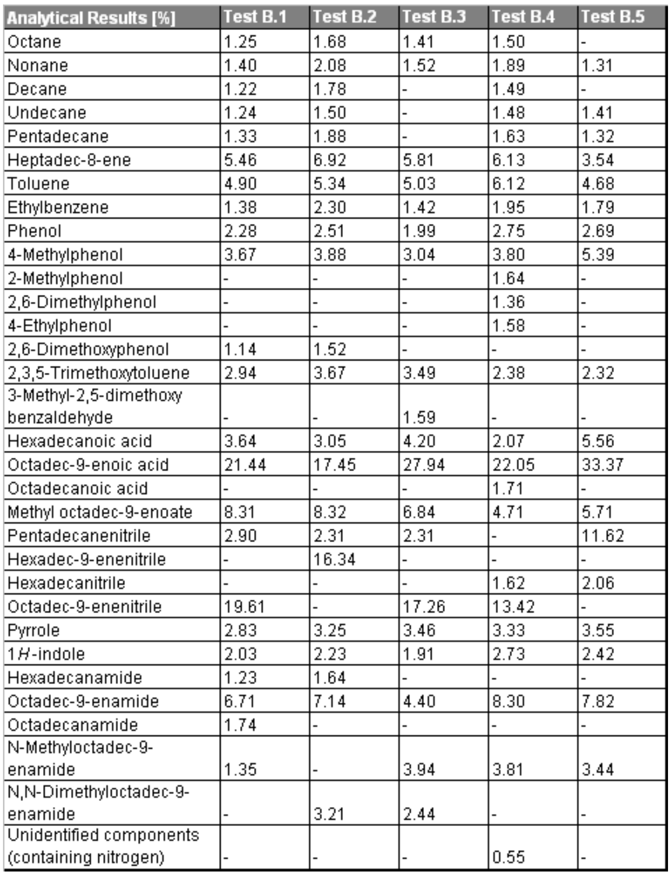
Table 8-6: Aqueous phase detailed composition of the performed rapeseed cake and safflower oil co-conversion tests



Analytical Results [%]	Test A.1	Test A.2	Test A.3	Test A.4	Test A.5	Test A.6	Test A.7
5-Isobutyl-3-methylphenol	-	-	2.95	-	-	-	-
Benzene-1,2-diol	-	-	3.72	3.83	1.93	-	2.99
Benzene-1,4-diol	-	-	1.53	1.50	-	-	-
3-Methoxybenzene-1,2-diol	-	-	1.84	1.95	1.13	-	2.34
Phenol	1.83	1.54	3.24	3.25	3.78	6.85	2.71
3-Methylphenol	-	-	-	1.67	-	-	-
4-Methylphenol	1.21	-	-	-	2.82	3.28	4.27
2,6-Dimethoxyphenol	2.84	2.98	1.79	2.07	2.79	4.89	2.91
2,3,5-Trimethoxytoluene	2.55	1.99	-	-	1.80	3.07	2.02
Dodecylphenol	1.41	-	-	-	-	-	-
Acetic acid	-	10.54	-	-	-	-	-
Propanoic acid	3.53	9.13	17.09	13.98	13.93	18.03	12.95
Isobutanoic acid	-	-	-	1.76	-	-	-
Butanoic acid	3.32	6.01	6.67	6.42	4.71	6.98	7.14
2-Methylbutanoic acid	-	-	-	-	-	-	2.69
3-Methylbutanoic acid	1.55	-	2.43	3.24	-	4.47	5.75
Pentanoic acid	2.32	4.41	6.44	5.04	1.74	-	3.63
4-Methylpentanoic acid	2.02	-	-	-	-	-	1.88
Hexanoic acid	-	2.10	1.65	1.71	1.95	-	3.68
Heptanoic acid	3.88	-	1.94	2.89	3.19	-	5.13
Hexadecanoic acid	6.44	-	-	-	-	-	-
Octadecenoic acid	2.88	-	-	-	-	-	-
Octadecanoic acid	1.76	-	-	-	-	-	-
Methyl Octadecenoate	0.44	-	-	-	-	-	-
Propanenitrile	-	1.63	-	-	-	-	-
Hexadecanenitrile	2.73	-	-	-	-	-	-
Octadecanenitrile	6.58	-	-	-	-	-	-
Butan-2-one	-	2.55	-	-	-	-	-
1-Hydroxypropan-2-one	2.90	4.58	-	-	-	-	-
Cyclopentanone	-	2.13	1.53	-	2.21	2.90	-
1-(Acetyloxy)propan-2-one	3.06	2.31	3.52	3.02	-	5.37	-
Pentan-3-one	-	-	-	2.47	-	-	-
2-Methylpentan-3-one	-	-	-	-	-	-	1.60
Cyclopent-2-en-1-one	1.38	-	-	-	1.37	-	-
3-Methylcyclopent-2-en-1-one	1.34	2.10	1.38	-	-	-	-
2-Hydroxy-3-methylcyclopent-2-en-1-one	-	-	-	-	2.08	-	2.11
Cyclohexanone	-	-	-	-	2.96	-	-
Hepten-2-al	-	-	1.40	-	-	-	-
But-3-en-2-ol	-	-	1.47	-	1.87	2.92	-
Pent-1-en-3- ol	-	1.02	-	-	-	-	-
Hex-2-en-1-ol	-	-	2.75	-	-	-	-
Furan-2-methanol	4.08	-	4.65	6.69	6.21	13.86	5.75
Tetrahydrofuran-2-one	2.89	2.51	4.06	2.04	2.03	2.11	-
2-Acetylfuran	2.86	2.41	-	2.14	1.50	-	-
Methyl 2-furancarboxylate	-	-	-	-	6.47	-	-
3-Hydroxy-2-methyl-4*H*-pyran-4-one	-	1.46	-	-	-	-	-
Pyrrol	-	-	-	-	1.78	2.48	-
Pyrazine	-	-	-	-	1.63	-	-
Pyridine	2.04	-	1.60	1.43	4.57	4.34	1.57
2-Methylpyridine	-	2.31	-	-	-	1.45	2.06
3-Methylpyridine	-	-	-	-	2.04	2.93	1.87
2-Methylpyrazine	-	-	-	1.49	2.49	1.77	1.41
2,6-Dimethylpyrazine	-	2.51	-	-	2.17	-	-
Pyrrolidin-2-one	3.71	7.36	-	-	-	-	-
Pyrrolidine-2,5-dione	2.85	1.58	3.73	1.83	-	-	1.53
1-Methylpyrrolidine-2,5-dione	2.68	5.10	4.47	1.97	2.21	-	1.67
3-Methylpyrrolidine-2,5-dione	8.43	11.35	-	4.20	2.94	-	2.76
1,3-Dimethylpyrrolidine-2,5-dione	-	-	-	-	-	-	1.68
Pyridin-4-ol	-	-	11.10	12.69	-	-	-
Pyridin-3-ol	-	-	-	2.23	9.51	9.32	14.10
3-Methylpyridin-4-ol	-	-	1.62	-	-	-	-
2,6-Piperidinedione	-	-	-	1.78	-	-	-
1-Methyl-2,6-Piperidinedione	-	2.77	-	-	2.27	2.98	-
6-Methylpyridin-3-ol	-	-	1.71	2.04	-	-	-
1,5-Dimethyl-2-pyrrolidinone	-	-	-	2.01	-	-	-
Hex-2-ene	-	-	-	2.66	-	-	-
Prop-2-enylcyclopentane	-	-	-	-	-	-	1.80
Pentadecane	1.98	-	-	-	-	-	-
Heptadec-8-ene	3.26	-	-	-	-	-	-
1-Methyldecylbenzene	0.83	-	-	-	-	-	-
1*H*-indole-2,3-diol		-	-	-	1.92	-	-
N,N-dimethylacetamide	1.88	1.02	-	-	-	-	-
3,9-Diazatricyclo-[7.3.0.0(3,7)]dodecan-2,8-dione	6.54	4.60	-	-	-	-	-
5-Methyl-2-mercaptopyridine	-	-	1.93	-	-	-	-
1-Methyl-3-methoxytriazole	-	-	1.79	-	-	-	-

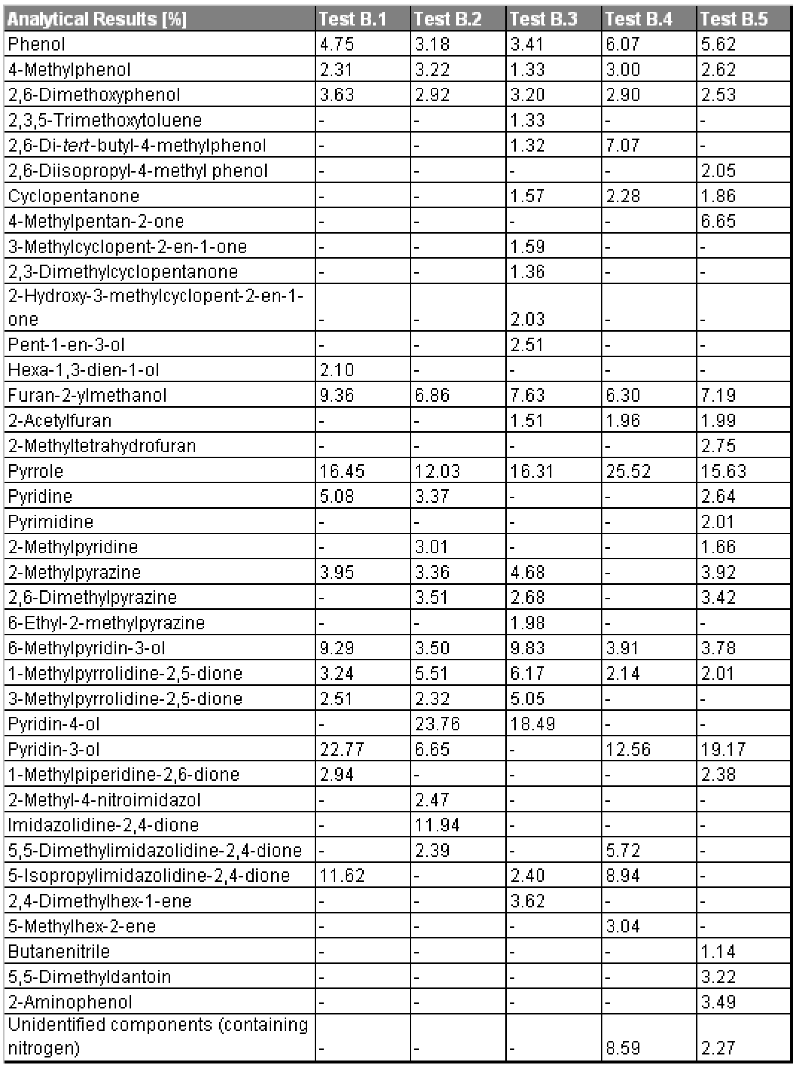
8.3.2 RAPESEED CAKE CONVERSION WITH TWO REACTOR CONFIGURATIONS

Table 8-7: Organic phase detailed composition of the rapeseed cake conversion tests using two reactor configurations



Analytical Results [%]	Test B.1	Test B.2	Test B.3	Test B.4	Test B.5
Octane	1.25	1.68	1.41	1.50	-
Nonane	1.40	2.08	1.52	1.89	1.31
Decane	1.22	1.78	-	1.49	-
Undecane	1.24	1.50	-	1.48	1.41
Pentadecane	1.33	1.88	-	1.63	1.32
Heptadec-8-ene	5.46	6.92	5.81	6.13	3.54
Toluene	4.90	5.34	5.03	6.12	4.68
Ethylbenzene	1.38	2.30	1.42	1.95	1.79
Phenol	2.28	2.51	1.99	2.75	2.69
4-Methylphenol	3.67	3.88	3.04	3.80	5.39
2-Methylphenol	-	-	-	1.64	-
2,6-Dimethylphenol	-	-	-	1.36	-
4-Ethylphenol	-	-	-	1.58	-
2,6-Dimethoxyphenol	1.14	1.52	-	-	-
2,3,5-Trimethoxytoluene	2.94	3.67	3.49	2.38	2.32
3-Methyl-2,5-dimethoxy benzaldehyde	-	-	1.59	-	-
Hexadecanoic acid	3.64	3.05	4.20	2.07	5.56
Octadec-9-enoic acid	21.44	17.45	27.94	22.05	33.37
Octadecanoic acid	-	-	-	1.71	-
Methyl octadec-9-enoate	8.31	8.32	6.84	4.71	5.71
Pentadecanenitrile	2.90	2.31	2.31	-	11.62
Hexadec-9-enenitrile	-	16.34	-	-	-
Hexadecanitrile	-	-	-	1.62	2.06
Octadec-9-enenitrile	19.61	-	17.26	13.42	-
Pyrrole	2.83	3.25	3.46	3.33	3.55
1*H*-indole	2.03	2.23	1.91	2.73	2.42
Hexadecanamide	1.23	1.64	-	-	-
Octadec-9-enamide	6.71	7.14	4.40	8.30	7.82
Octadecanamide	1.74	-	-	-	-
N-Methyloctadec-9-enamide	1.35	-	3.94	3.81	3.44
N,N-Dimethyloctadec-9-enamide	-	3.21	2.44	-	-
Unidentified components (containing nitrogen)	-	-	-	0.55	-

Table 8-8: Aqueous phase detailed composition of the rapeseed cake conversion tests using two reactor configurations



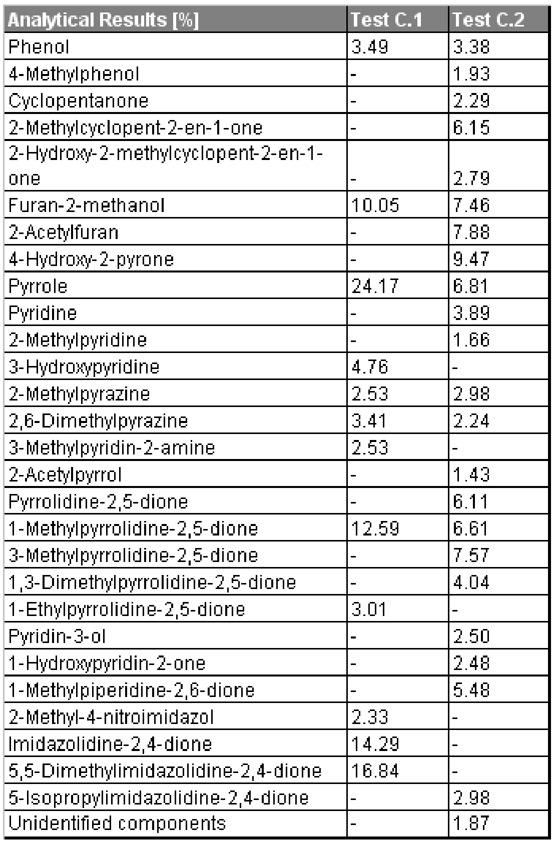
Analytical Results [%]	Test B.1	Test B.2	Test B.3	Test B.4	Test B.5
Phenol	4.75	3.18	3.41	6.07	5.62
4-Methylphenol	2.31	3.22	1.33	3.00	2.62
2,6-Dimethoxyphenol	3.63	2.92	3.20	2.90	2.53
2,3,5-Trimethoxytoluene	-	-	1.33	-	-
2,6-Di-*tert*-butyl-4-methylphenol	-	-	1.32	7.07	-
2,6-Diisopropyl-4-methyl phenol	-	-	-	-	2.05
Cyclopentanone	-	-	1.57	2.28	1.86
4-Methylpentan-2-one	-	-	-	-	6.65
3-Methylcyclopent-2-en-1-one	-	-	1.59	-	-
2,3-Dimethylcyclopentanone	-	-	1.36	-	-
2-Hydroxy-3-methylcyclopent-2-en-1-one	-	-	2.03	-	-
Pent-1-en-3-ol	-	-	2.51	-	-
Hexa-1,3-dien-1-ol	2.10	-	-	-	-
Furan-2-ylmethanol	9.36	6.86	7.63	6.30	7.19
2-Acetylfuran	-	-	1.51	1.96	1.99
2-Methyltetrahydrofuran	-	-	-	-	2.75
Pyrrole	16.45	12.03	16.31	25.52	15.63
Pyridine	5.08	3.37	-	-	2.64
Pyrimidine	-	-	-	-	2.01
2-Methylpyridine	-	3.01	-	-	1.66
2-Methylpyrazine	3.95	3.36	4.68	-	3.92
2,6-Dimethylpyrazine	-	3.51	2.68	-	3.42
6-Ethyl-2-methylpyrazine	-	-	1.98	-	-
6-Methylpyridin-3-ol	9.29	3.50	9.83	3.91	3.78
1-Methylpyrrolidine-2,5-dione	3.24	5.51	6.17	2.14	2.01
3-Methylpyrrolidine-2,5-dione	2.51	2.32	5.05	-	-
Pyridin-4-ol	-	23.76	18.49	-	-
Pyridin-3-ol	22.77	6.65	-	12.56	19.17
1-Methylpiperidine-2,6-dione	2.94	-	-	-	2.38
2-Methyl-4-nitroimidazol	-	2.47	-	-	-
Imidazolidine-2,4-dione	-	11.94	-	-	-
5,5-Dimethylimidazolidine-2,4-dione	-	2.39	-	5.72	-
5-Isopropylimidazolidine-2,4-dione	11.62	-	2.40	8.94	-
2,4-Dimethylhex-1-ene	-	-	3.62	-	-
5-Methylhex-2-ene	-	-	-	3.04	-
Butanenitrile	-	-	-	-	1.14
5,5-Dimethyldantoin	-	-	-	-	3.22
2-Aminophenol	-	-	-	-	3.49
Unidentified components (containing nitrogen)	-	-	-	8.59	2.27

8.3.3 MEAT MEAL C1 AND ALGAE CONVERSION

Table 8-9: Organic phase detailed composition of the separate meat meal C1 and algae conversion tests

Analytical Results [%]	Test C.1	Test C.2
Octane	-	1.71
Nonane	1.40	2.07
Non-1-ene	-	1.33
Decane	1.75	2.58
Dec-1-ene	-	1.41
Undecane	-	3.11
Undec-1-ene	4.04	1.65
Dodecane	2.06	3.54
Dodec-1-ene	-	1.71
Tridecane	2.19	6.80
Tridec-1-ene	-	1.92
Tetradecane	2.07	5.86
Tetradec-1-ene	-	2.95
Cyclopentadecane	-	8.02
Pentadecane	3.57	18.83
Pentadec-1-ene	-	2.85
Hexadecane	1.70	2.25
Heptadecane	-	3.82
Heptadec-8-ene	4.25	-
Toluene	4.75	3.21
Ethylbenzene	2.67	-
Vinylbenzene	1.32	-
Phenol	3.77	-
4-Methylphenol	2.90	-
Hexadecanoic acid	2.54	5.46
Hexadecenoic acid	-	3.92
Octadec-9-enoic acid	2.09	-
Octadecanoic acid	1.40	-
Palmitic acid methyl ester	-	1.23
Methyl octadecanoate	-	1.42
3-Methylbutanenitril	1.62	-
Hexadec-9-enenitrile	-	4.23
Hexadecanitrile	9.24	8.12
Octadecanenitrile	8.09	-
Octadec-9-enenitrile	11.28	-
Pyrrole	6.34	-
3-Methyl-1*H*-pyrrol	3.15	-
2-Ethyl-1*H*-pyrrol	2.19	-
3-Ethyl-4-methylpyrrole	1.61	-
1*H*-indole	1.84	-
Hexadecanamide	4.33	-
Octadec-9-enamide	4.16	-
N-Methyloctadec-9-enamide	1.68	-

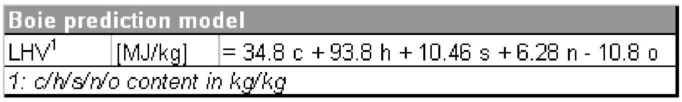
Table 8-10: Aqueous phase detailed composition of the separate meat meal C1 and algae conversion tests



Analytical Results [%]	Test C.1	Test C.2
Phenol	3.49	3.38
4-Methylphenol	-	1.93
Cyclopentanone	-	2.29
2-Methylcyclopent-2-en-1-one	-	6.15
2-Hydroxy-2-methylcyclopent-2-en-1-one	-	2.79
Furan-2-methanol	10.05	7.46
2-Acetylfuran	-	7.88
4-Hydroxy-2-pyrone	-	9.47
Pyrrole	24.17	6.81
Pyridine	-	3.89
2-Methylpyridine	-	1.66
3-Hydroxypyridine	4.76	-
2-Methylpyrazine	2.53	2.98
2,6-Dimethylpyrazine	3.41	2.24
3-Methylpyridin-2-amine	2.53	-
2-Acetylpyrrol	-	1.43
Pyrrolidine-2,5-dione	-	6.11
1-Methylpyrrolidine-2,5-dione	12.59	6.61
3-Methylpyrrolidine-2,5-dione	-	7.57
1,3-Dimethylpyrrolidine-2,5-dione	-	4.04
1-Ethylpyrrolidine-2,5-dione	3.01	-
Pyridin-3-ol	-	2.50
1-Hydroxypyridin-2-one	-	2.48
1-Methylpiperidine-2,6-dione	-	5.48
2-Methyl-4-nitroimidazol	2.33	-
Imidazolidine-2,4-dione	14.29	-
5,5-Dimethylimidazolidine-2,4-dione	16.84	-
5-Isopropylimidazolidine-2,4-dione	-	2.98
Unidentified components	-	1.87

8.4 HEATING VALUES PREDICTION MODELS

Table 8-11: The heating value prediction model by Boie



Boie prediction model		
LHV[1]	[MJ/kg]	$= 34.8\ c + 93.8\ h + 10.46\ s + 6.28\ n - 10.8\ o$
1: c/h/s/n/o content in kg/kg		

8.5 SAMPLE PHOTOS OF THE LIQUID FUEL SAMPLES

Figure 8-1. Sample photos of (a) the organic and (b) the aqueous phase

8.6 CHROMATOGRAMS EXAMPLE OF THE LIQUID PRODUCT SAMPLES

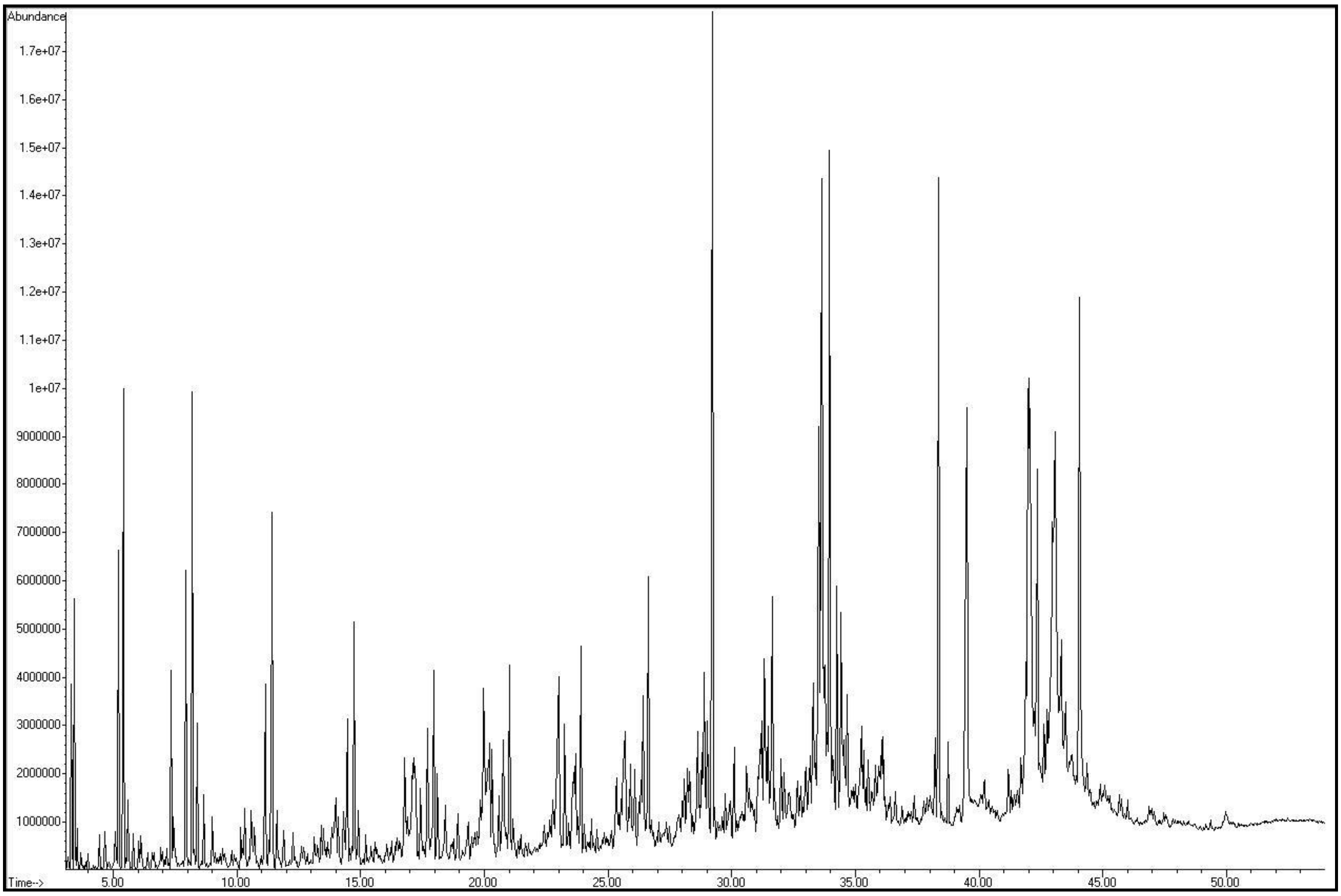


Figure 8-2. Chromatogram example of the organic phase

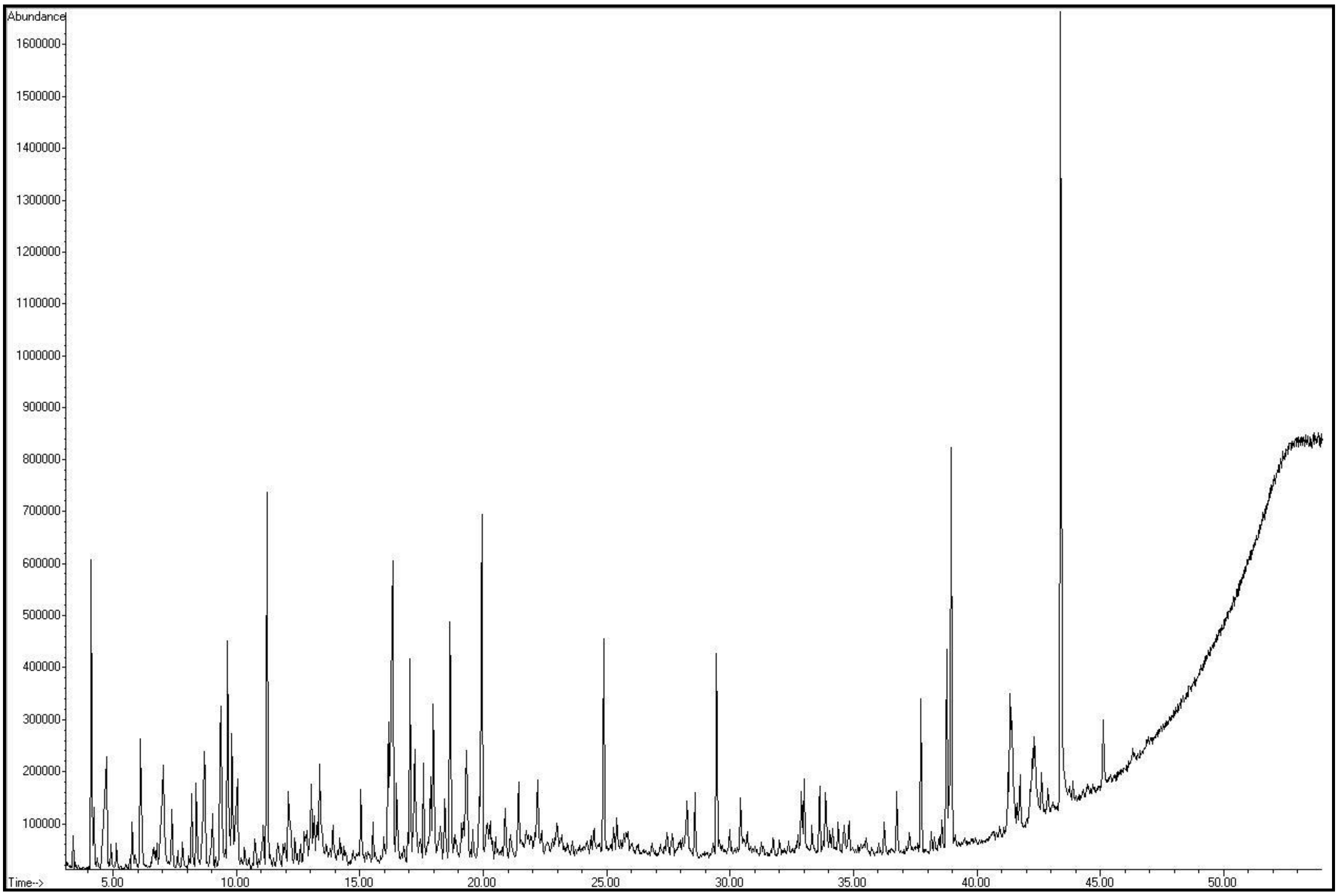


Figure 8-3. Chromatogram example of the aqueous phase

8.7 XRD SPECTRUM EXAMPLE OF THE REGENERATED CATALYST

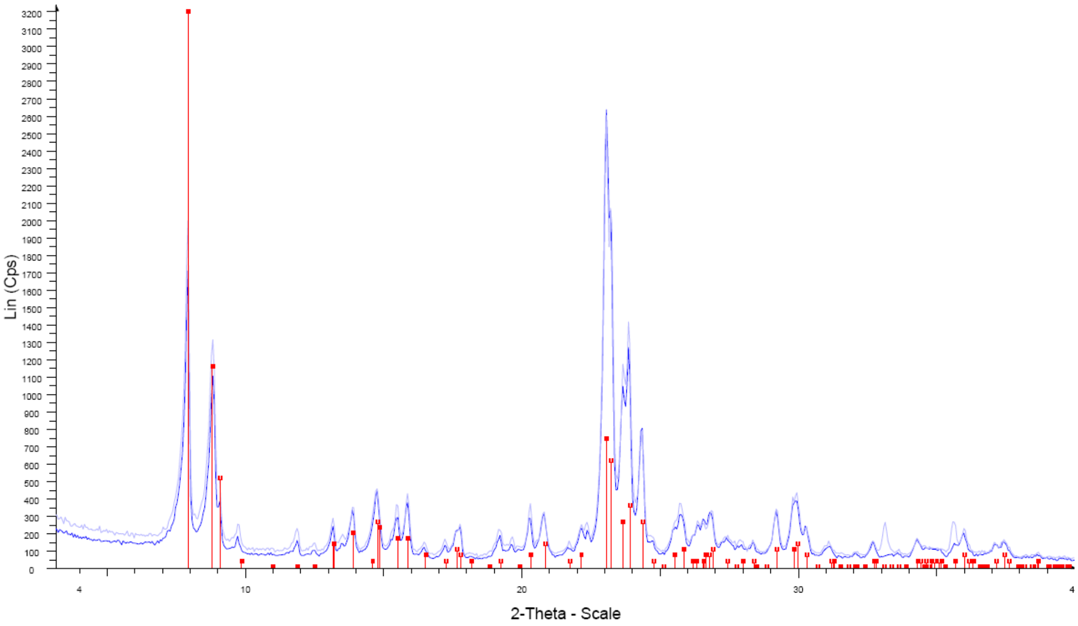


Figure 8-4. XRD spectrum example of the regenerated catalyst

8.8 SAMPLE PHOTOS OF THE CATALYST BEFORE AND AFTER REGENERATION

Figure 8-5. Sample photos of the catalyst (a) before and (b) after regeneration

8.9 PUBLISHED PAPERS AT SCIENTIFIC JOURNALS

1. Giannakopoulou, K., Lukas, M., Vasiliev, A., Brunner, C., Schnitzer, H., 2009, Low pressure co-conversion of biogenic waste (rapeseed cake) and vegetable oil, Bioresource Technology, doi:10.1016/j.biortech.2009.12.032

2. Giannakopoulou, K., Lukas, M., Vasiliev, A., Brunner, C., Schnitzer, H., 2010, Conversion of rapeseed cake into bio-oils in a batch reactor: effect of catalytic vapour upgrading, Microporous and Mesoporous Materials 128, 126-135

8.10 PRESENTATIONS AND PUBLIC EVENTS

The results of this study were presented at the following conferences/public events:

1. 16th Biomass Conference and Exhibition, 1-6/6/2008, Valencia, Spain
2. Advances in Energy Studies, 6th Biennial International Workshop, 29/6-2/7/2008, Graz, Austria
3. National IEA Bioenergy Workshop, 9/9/2008, Vienna, Austria
4. 4th International Symposium on the Environment, AT.IN.E.R., 21-24/5/2009, Athens, Greece

KANELLINA GIANNAKOPOULOU

Personal Information

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Marital status	Single
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Profile

Highly motivated individual, with leadership, organizing, and problem-solving skills. With good technical background in chemical engineering issues. Competent in observing, comparing, analyzing and planning. Able to cooperate and communicate efficiently with others. Decisive and hard-working.

Education

Dates	Oct. 2006 – March. 2010

PhD thesis: “Development of a low pressure, catalytic process for the production of biofuels”, Graz University of Technology, Graz, Austria

Design of the catalytic process, construction of a laboratory-scale testing facility, performance of systematic tests with different feedstocks and catalysts, preparation of a feasibility study for the upscaling of the developed process.

Dates	Oct. 1999 – Feb. 2005

Diploma in Chemical Engineering, National Technical University of Athens, Athens, Greece

Focus on Process Analysis and Design. The Diploma Thesis included research and experimental work about the “Use of cerium catalysts for the Water-Gas Shift reaction”.

Professional experience

Dates	Jul. 2005 – Dec. 2005
	Internship at Joanneum Research, at the Institute of Sustainable Techniques and Systems, Graz, Austria
	Research work in the field of synthetic fuels, solar thermal energy, energy efficiency and market research for the development of new products.
Dates	Sept. 2003 – Oct. 2003
	Internship at the Department of Operations, Engineering and HSSE of Shell-Gas, Aspropyrgos, Greece
	Familiarization with the safety rules and technical specifications of constructing domestic / industrial LPG facilities and of the delivering / storage / distribution of LPG.
Dates	Apr. 2003 – May 2003 and Oct. 2004 – Dec. 2004
	Member of the research team “Development and Application of Quality Control Systems at Fuels Stations in Greece” ELIN Fuels in co-operation with the National Technical University of Athens, Athens, Greece
	Sampling of liquid fuels from fuel stations in West Peloponnese and quality testing at the Laboratory of Fuels and Lubricants of the National Technical University of Athens.

Languages

Greek	Native speaker
English	Excellent skills:
	(1) Certificate of Proficiency in English, Cambridge University, Dec. 2000
	(2) Qualification of Adequacy for the English Language, Greek Ministry of Education
German	Intermediate speaking and writing skills
Computer Skills	Microsoft Office (Word, Excel, Powerpoint, Visio), Photoshop, Mathcad, Matlab, Fortran

Seminars

Creativity Techniques (2008),

Innovation for Sustainability in Industry (2008),

Ecological Process Evaluation (2007),

Renewable Resources-Production Technologies (2007),

Production Integrated Environmental Protection (2007)

at the Graz University of Technology, Graz, Austria.

Renewable Energy Resources (2006)

at the Halmstad University, Falkenberg, Sweden

Interests

Special interest in arts: ballet (10 years), traditional greek dance (4 years), opera singing (3 years), music, theatre, cinema. Also, travelling and psychology.

Publications

Scientific Journals

(1) K. Giannakopoulou, M. Lukas, A. Vasiliev, C. Brunner, H. Schnitzer, “Low pressure co-conversion of biogenic waste (rapeseed cake) and vegetable oil”, Bioresource Technology, , doi:10.1016/j.biortech.2009.12.032

(2) K. Giannakopoulou, M. Lukas, A. Vasiliev, C. Brunner, H. Schnitzer, “Conversion of rapeseed cake into bio-oils in a batch reactor: effect of catalytic vapor upgrading”, Microporous and Mesoporous Materials 128 (2010) 126-135

Conferences

(1) K. Giannakopoulou, M. Lukas, S. Scober, M. Mittelbach, B. Slawitsch, H. Boechzelt, C. Brunner, H. Schnitzer, “Low pressure, catalytic depolymerization of biogenic feedstocks”, 16th Biomass Conference and Exhibition, 1-6/6/2008, Valencia, Spain

(2) K. Giannakopoulou, M. Lukas, S. Scober, M. Mittelbach, B. Slawitsch, H. Boechzelt, C. Brunner, H. Schnitzer, “Development of a Low Pressure, Catalytic, Direct Liquefaction Process for the Conversion of Biogenic Materials into Liquid Fuels”, Advances in Energy Studies, 6th Biennial International Workshop, 29/6-2/7/2008, Graz, Austria

(3) K. Giannakopoulou, C. Brunner, “Low Pressure, Catalytic Conversion of Biogenic Feedstocks”, National IEA Bioenergy Workshop, 9/9/2008, Vienna,

Austria

(4) K. Giannakopoulou, C. Brunner, H. Schnitzer, “Low Pressure, Catalytic Conversion of Biogenic Materials into Liquid Biofuels: Effect of Zeolite Catalysts”, 4th International Symposium on the Environment, 21-24/5/2009, Athens, Greece

Conferences Attended

(1) 3rd Panhellenic Conference of Chemical Engineering, NATIONAL TECHNICAL UNIVERSITY OF ATHENS, 31/5-2/6/2001, Athens, Greece

(2) “Waste utilization in favor of Humans”, FESTIVAL FOITHSH, 22-23/11/2003, Athens, Greece

(3) Biofuel Marketplace International Workshop and Stakeholder Event, INTELLIGENT ENERGY EUROPE, 9/3/2006, Budapest, Hungary

(4) Environmental Management Accounting and Cleaner Production (EMAN/CP), GRAZ UNIVERSITY OF TECHNOLOGY, 26/4/2006, Graz, Austria

(5) World Biofuel Markets, GREEN POWER CONFERENCES, 12-14/3/2008, Brussels, Belgium

(6) 16th Biomass Conference and Exhibition, ETA-Florence Renewable Energies, 1-6/6/2008, Valencia, Spain

(7) Advances in Energy Studies, 6th Biennial International Workshop, GRAZ UNIVERSITY OF TECHNOLOGY, 29/6-2/7/2008, Graz, Austria

(8) National IEA Bioenergy Workshop, IEA AUSTRIA, 9/9/2008, Vienna, Austria

(9) “Moving towards a future with Renewable Energy Sources”, GREEK WOMAN’S ENGINEERING ASSOCIATION, 4/3/2009, Athens, Greece

(10) “Improvement of the Energy Efficiency in Industry, Buildings, Transportation”, GREEK WOMAN’S ENGINEERING ASSOCIATION, 5/3/2009, Athens, Greece

(11) 4th International Symposium on the Environment, AT.IN.E.R., 21-24/5/2009, Athens, Greece

Associations

(1) Member of T.E.E. (Technical Chamber of Greece)

(2) Member of E.D.E.M. (Greek Woman’s Engineering Association)

(3) Member of AT.IN.E.R. (The Athens Institute for Education and Research)

Scholarships	(1) From “Korgialleneion Athlon” for support during the PhD studies, 10/2006-9/2009
	(2) From I.K.Y. (State Scholarships Foundations) for high academic achievement, 10/1999-6/2000