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Hoffmann, Jessica

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Bio-oil Production - Process Optimization and Product Quality

Jessica Hoffmann

Dissertation submitted to the Faculty of Engineering and Science at
Aalborg University in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Aalborg University
Department of Energy Technology

October, 2013
Aalborg, Denmark

To my family

Abstract

The concurrent increase in global primary energy demand by an annual 1.8% (2012) (1) and depletion of conventional resources combine with climate issues and the desire for national/regional energy independence to lead to an urgent need for renewable as well as sustainable energy sources. In 2012, fossil fuels still accounted for 87% of global and 81% of EU primary energy consumption (1). In an effort to reduce the carbon footprint of a continued supply of liquid fuels, processes utilizing biomass in general, and lignocellulosic biomass in particular, are being developed to replace their fossil counterparts (2). For some sectors of transportation, notably the marine, aviation and heavy duty land transport sectors, sustainably produced biofuels seem to be the most promising pathway in the near and medium term. This is especially so, if the biofuels possess drop-in properties, i.e. are completely miscible with the existing hydrocarbon fuel at the drop-in point in such a way that neither logistics nor end user technology must be replaced in order to accommodate the increasing blend fraction of biofuels. However, as biomass will also become the primary feedstocks for carbon containing chemicals, plastics, nutritional and pharmaceutical products, it will become a high-cost commodity. Therefore it is of great importance to develop a sustainable and marketable process for the conversion of biomass, which is feedstock flexible and energy efficient and offers high conversion efficiency. Only a process like this has the ability to produce a drop-in product that is commercially compatible to conventional fuels as wells as has the capability to endure. Furthermore, liquid biofuels in future need to be produced in bulk to meet demand; thus, the challenge becomes one of finding the right process with high feedstock flexibility. One such candidate is hydrothermal liquefaction (HTL), a thermochemical process that converts low-value biomass feedstocks to a high-value bio-through the use of hot compressed water and catalysts. As there is typically residual oxygen left in the bio-crude from HTL, further processing involves upgrading in order to be further treated in existing refineries. The design of an efficient, low input procedure for this requires an accurate understanding of the nature of the bio-crude along with corresponding upgrading pathways as well as existing refinery structure assessment. Once pathways have been identified the optimal configuration for refining can be designed. Figure 1 visualise the pathways from biomass feedstock to refinery drop-in fuel.

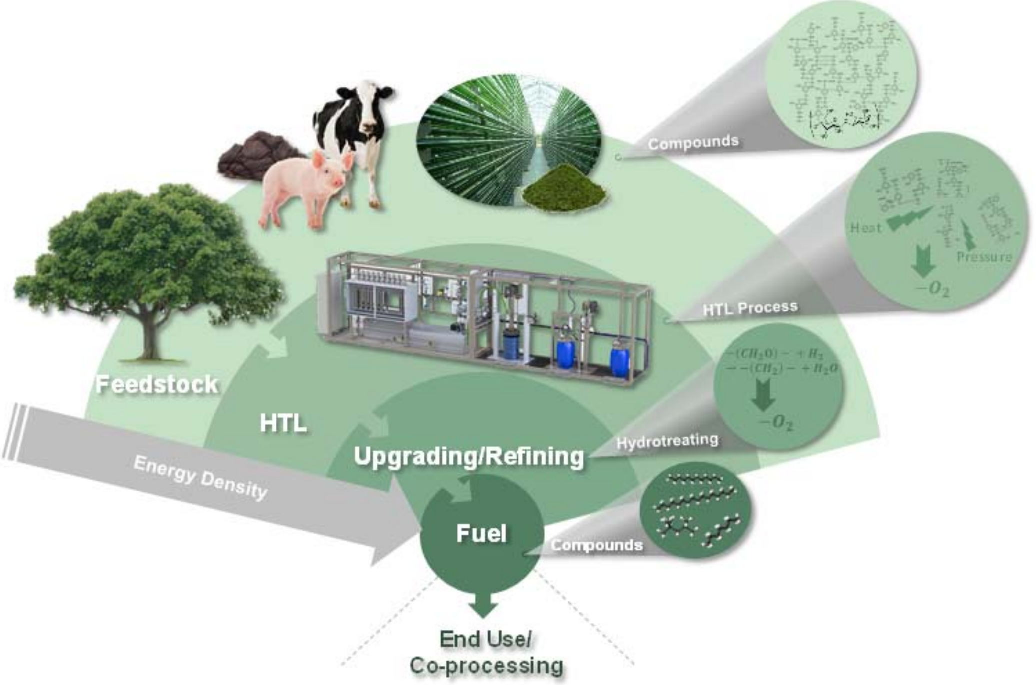


Figure 1: Process scheme – from feedstock to advanced biofuel [Publication B].

Resumé

Den samtidige stigning i det globale primære energibehov med årligt 1,8% (2012) (1) og forbrug af endelige konventionelle ressourcer kombineret med klimaspørgsmål og ønsket om national / regional energiuafhængighed fører til et presserende behov for vedvarende samt bæredygtige energikilder. I 2012, udgjorde fossile brændstoffer stadig 87 % af det globale og 81% af EUs primære energiforbrug (1). I et forsøg på at reducere carbon footprint af en fortsat forsyning af flydende brændstoffer udvikles processer til at udnytte biomasse generelt, og lignocellulosisk biomasse i særdeleshed til at erstatte deres fossile modstykker (2). For nogle dele af transportsektoren, særligt marine, luftfart og tung landtransport, synes bæredygtigt produceret biobrændstof at være den mest lovende vej på kort og mellemlangt sigt. Dette er især tilfældet, hvis biobrændstoffer besidder drop-in egenskaber, dvs. er fuldstændigt blandbare med den eksisterende kulbrinte brændstof på drop-in punkt på en sådan måde, at hverken logistik eller slutbruger teknologi skal udskiftes for at imødekomme en stigende iblanding af biobrændstoffer. Dog vil biomasse også blive det primære råmateriale for kulstof-indeholdende kemikalier, plast, ernæringsmæssige og farmaceutiske produkter, og derfor vil det blive en high- cost handelsvare. Derfor er det af stor betydning at udvikle en bære-dygtigt og salgbar proces til omdannelse af biomasse, som er råmateriale fleksibel, energieffektiv og giver høj virkningsgrad. Kun en proces som denne har evnen til at producere et drop-in produkt, der er kommercielt kompatibel med konventionelle. Da stadigt mere flydende biobrændsel i fremtiden skal masseproduceres for at imødekomme efterspørgslen, ligger der dermed en udfordring i at finde den rigtige proces med stor råvare fleksibilitet. En sådan kandidat er hydrotermisk liquefaction (HTL), en termokemisk proces, der omdanner lav-værdi biomasseråmaterialer til en høj værdi bio-crude hjælp af varmt komprimeret vand og katalysatorer. Da der typisk er tilbageværende oxygen tilbage i bio-cruden fra HTL, er det nødvendigt at videreforarbejde dette, igennem opgradering for at blive yderligere behandlet i eksisterende raffinaderier. Udformningen af en effektiv, lavt input procedure for dette kræver en præcis forståelse af karakteren af bio-cruden sammen med tilsvarende opgraderingsruter samt en sammenlignende vurdering af den eksisterende raffinaderi struktur. Når opgraderingsruterne er blevet identificeret kan den optimale konfiguration til raffinering udformes. Figur 1 visualiserer veje fra biomasse råmateriale til raffineret drop-in brændstof.

Acknowledgements

"Curiouser, curiouser" – Alice in Wonderland

… and like Alice I finally found my way out of the rabbit hole, but it wasn't just a dream, but as well a time full of adventures, challenging, with its ups and downs, but at the same time very rewarding. An experience, that made me *grow* and I would not want to miss it. Of course my time in *"Wonderland"* would not have been possible without the support of my family and friends, who guided me, when I wasn't sure *"which way I ought to go".* And just like the Cheshire Cat, they always had good advice, made me laugh and continue my path the right direction. I am very thankful for this.

Of course I would also like to express my sincere gratitude to my supervisor Lasse Rosendahl, who showed me which part of the mushroom to eat *to grow taller* ☺. I very much appreciate his help, discussing and reviewing my work, and giving me valuable feedback and some of his enthusiasm.

Lastly, I would thank my colleagues at the department and the department itself, for the great working environment they provided and all of those who supported me in any respect during the completion of the project.

Aalborg, 17th of October, 2013 *Jessica Hoffmann*

Contents

Preface

This thesis is submitted as partial fulfilment of the requirements for the degree of Doctor of Philosophy at Aalborg University, Denmark. The main part of the thesis is a collection of papers published in or submitted to peer-reviewed journals. It is the results of three years of research at the Department of Energy Technology, Aalborg University, in the period August 2010 - October 2013. The contributions to this thesis were done under the supervision of Professor Lasse A. Rosendahl to whom I would like to express my sincere gratitude for sharing his expertise and enthusiasm. The work has been done under the financial support of the Center for Energy Materials from the Strategic Research Council of Denmark under grant no. 823032, for which I am very grateful. A close collaboration with Steeper Energy Aps and Canmet Energy, Natural Resources Canada has been initiated. Throughout this collaboration, the high quality knowledge of Steen Brummerstedt Iversen, Jinwen Chen and Edward Little has been a great inspiration. And I highly appreciate their support and advice.

List of Publications

This dissertation is a collection of scientific papers based on the Ph.D. project objectives set during the research work to advance scientific and industrial goals. Most of the details of this research study are contained in the attached papers and therefore the presented manuscript should be intended only as a summary of the overall project. This study is the outcome of my research as a PhD student at the Department of Energy Technology, Aalborg University, Denmark from August 2010 to October 2013. The work has resulted in three journal papers, one book chapter and several conference contributions listed below:

A. **Conceptual design of an integrated hydrothermal liquefaction and biogas plant for sustainable bioenergy production.** / Hoffmann, Jessica; Rudra, Souman; Toor, Saqib; Holm-Nielsen, Jens Bo; Rosendahl, Lasse.
I: Bioresource Technology, Vol. 129, 02.2013, s. 402-410.

B. **Preliminary Results for Upgrading of Biocrude from Hydrothermal Liquefaction** / Jessica Hoffmann, Steen B. Iversen, Thomas H. Pedersen, Lasse A. Rosendahl
I: Submitted to Environmental Progress and Sustainable Energy Journal

C. **Hydrothermal Conversion in near-critical water - A sustainable way of producing renewable fuel** / Jessica Hoffmann, Thomas Helmer Pedersen, Lasse Aistrup Rosendahl
I: Submitted to Biorefineries . red. / Zhen Fang. Springer, 2013.

D. **Upgrading of Bio-crude from Hydrothermal Liquefaction** / Jessica Hoffmann, Lasse A. Rosendahl I: Oral presentation at 3rd Thermochemical Biomass Conference 2013, Chicago, Illinois, USA.

E. Process Optimization of an Integrated Hydrothermal Liquefaction and Biogas Plant for Sustainable Bioenergy Production / Jessica Hoffmann, Lasse A. Rosendahl
I: Oral presentation at the Sustainable Energy Technology Conference 2012, Vancouver, Canada.

In addition to the main papers, the following publications have also been made during the Ph.D. project. They address further fundamental challenges of hydrothermal liquefaction:

i. **Lignocellulosic biomass-Thermal pretreatment with steam: Pretreatment techniques for biofuels and biorefineries.** / Toor, Saqib; Rosendahl, Lasse; Hoffmann, Jessica; Holm-Nielsen, Jens Bo; Ehimen, Ehiazesebhor Augustine.

I: Pretreatment Techniques for Biofuels and Biorefineries . red. / Zhen Fang. Springer, 2013.

ii. **Hydrothermal liquefaction of Spirulina and Nannochloropsis Salina under subcritical and supercritical water conditions.** / Toor, Saqib; Reddy, H. ; Deng, S.; Hoffmann, Jessica; Spangsmark, D.; Madsen, L. B.; Holm-Nielsen, Jens Bo; Rosendahl, Lasse.
I: Bioresource Technology, Vol. 131, 2013, s. 413-419.

iii. **Hydrothermal liquefaction of biomass: Application of hydrothermal reactions to biomass conversion.** / Toor, Saqib; Rosendahl, Lasse; Hoffmann, Jessica; Nielsen, Rudi P.; Pedersen, Thomas Helmer; Søgaard, Erik Gydesen.
I: Application of hydrothermal reactions to biomass conversion. red. / Fangming Jin. Springer, 2013.

This present report combined with the above listed scientific papers has been submitted for assessment in partial fulfilment of the PhD degree. The scientific papers are not included in this version due to copyright issues. Detailed publication information is provided above and the interested reader is referred to the original published papers. As part of the assessment, co-author statements have been made available to the assessment committee and are also available at the Faculty of Engineering and Science, Aalborg University.

Chapter 1 Introduction

Dependency on depleting fossil energy sources and concurrent rising global energy consumption and greenhouse gas emissions are triggering the urgent need for renewable and sustainable energy solutions. Also governmental policies, CO_2 pricing in some regions and continuously rising fossil fuel prices are eliciting the necessity for the development of sustainable energy sources. In 2009 global energy consumption summed up to 12.150 million tonnes of oil equivalent (Mtoe) of which 33 % is the share from oil, until 2035 oil demand will rise 18% driven by the transportation sector (3). New and alternative solutions have to be developed to secure world's energy supply.

Biomass as energy resource could be an essential player in resolving the world energy challenge. According to the World Energy Outlook 2012 New Policy Scenario (3) biomass resources are sufficient to meet projected demands without competing with food production, nonetheless eventual land-use implications, direct and indirect, have to be dealt with in a sustainable manner. The transportation sector is highly challenging, particularly because heavy duty and long distance transport is unlikely to be electrified in the coming decades. Furthermore modern engines and environmental restriction demand clean and efficient fuels.

Together with other renewable sources of energy such as wind and solar, biomass is expected to be one of the main pillars of the future energy system in the near and medium term. In order to provide a smooth transition, technologies utilizing biomass for fuels and chemicals are under heavy development around the world. It is to be expected, that as oil reserves become depleted, biomass will gradually cover the needs of the transport sector for liquid fuels, with the main application in maritime, heavy land and aerial transport. However, this will be in competition with biomass use for food, feed, polymers and high-value chemicals. As large quantities of biofuels are required, it is paramount to identify resource efficient pathways from feedstocks (including low value waste streams) to desired biofuels and other bio-products, and most importantly processes that ensure high energy, low cost, efficiency and sustainability of the biomass to fuel conversion process.

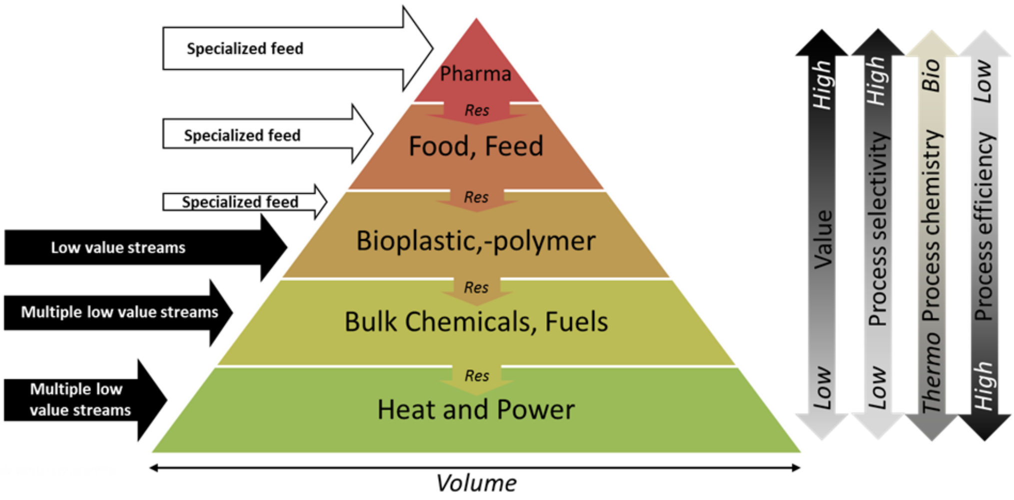


Figure 2: Biomass valorisation pyramid (Res=Residue)

Biomass can be used as an energy and chemical source in a range of different ways: it can be burned directly for the production of heat and power, biochemically digested or fermented or thermochemically converted to a liquid energy carrier. Research in biomass conversion technologies is extensive, and the challenge is to find technologies that are sustainable and therefore have the capacity to endure, even without governmental subsidies. When looking at biomass in a biorefinery concept, some biomass conversion routes need a lower quality input stream then other but therefore produce a product of a higher value. This is indicated in Figure 2 through the biomass valorisation pyramid, where technologies focussing on high value, low volume products are at the top, and technologies for low value, high volume products are at the bottom. For example, biomass streams used for pharmachemical production have to be narrowly selected, but residues from the conversion process can still be used for production of products lower in the cascade. Such high value product processes are typically both feedstock selective and deliver small volumes, resulting in high residual flow (or low resource efficiency), and are mostly based on biochemical pathways. Thermochemical processes, on the other hand, can convert various biomass feed streams, including low-value residual streams, and produce bulk chemicals, fuels, heat and power in high volumes but with lower value. Therefore, when operating at this end of the pyramid, processes must be highly efficient and flexible to be able to meet cost limitations on feedstock and operational costs.

This work focuses on thermochemical means of converting biomass to a liquid transportation fuel through hydrothermal liquefaction (HTL), and pays particular attention to the steps involved in getting from an HTL bio-crude to a drop-in fuel. Hydrothermal Liquefaction represents a technology, which is feedstock insensitive, energy-, cost- and feedstock-effective, with a high potential for sustainability and product flexibility with significant drop-in fuel capabilities making it a strong contender in the field of cost-effective bio-fuel production technologies. Furthermore, its feedstock insensitivity creates a range of potential synergies with other bio-fuel platforms. Goal hereby is to convert low-energy density biomass to a liquid high-energy fossil fuel like energy carrier.

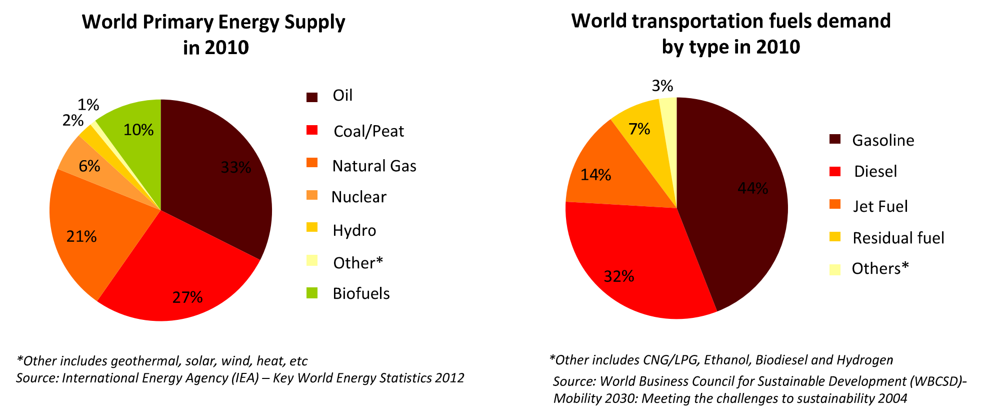
1.1 Energy Outlook

In 2011 31.2 Gt CO_2 have been released world-wide by fossil fuel combustion, which is equivalent to 60% of global greenhouse gas emission. Continuing like this would lead to an average global temperature increase of 5.3°C until 2035, regarding a scenario in the World energy Outlook 2012 (3).

Besides the need of reducing greenhouse gas emission, dependency on depleting fossil fuel sources needs to be reduced. When considering the transportation sector, fossil oil proven reserves allowing for a supply of 55 years at 2011's rates of production.

Additionally, the International Energy Outlook 2013 (4) estimates an increase of world energy consumption from 523 EJ in 2010 to 665 EJ in 2020 and 865 EJ in 2040 which means a 56% increase between the years 2010 - 2040. The total energy consumption increases 1.5% per year, mostly related to economic and population growth. Liquid fuel consumption for transportation increases with an annual rate of 1.1 % from 2010 to 2040. In the EU more than half of the final energy in the EU, while a quarter of final energy is consumed by households (5).

Figure 1 show the world primary energy supply by source for 2010. In 2010 major energy supply source came from fossil oil. Looking at the transport sector diesel and gasoline fuels have the biggest share of overall demand.



**Other includes geothermal, solar, wind, heat, etc*
Source: International Energy Agency (IEA) – Key World Energy Statistics 2012

**Other includes CNG/LPG, Ethanol, Biodiesel and Hydrogen*
Source: World Business Council for Sustainable Development (WBCSD)-Mobility 2030: Meeting the challenges to sustainability 2004

Figure 3: World energy supply by source and fuel demand for 2010, adapted from (4)

The 2010 progress report of the European Union on the Renewable Energy Directive (6) is emphasising the need for non-food feedstocks for the production of biofuels, inhibiting indirect land use change. Land-use change leads to reduced greenhouse gas savings of 1st generation, food-based bio-fuels in the overall life-cycle analysis. These facts support the need for the continued development of biomass to biofuel processes that are feedstock flexible and can handle 2nd and 3rd generation biomass.

1.2 Biomass

Biomass can be defined as organic matter of plant or animal origin. It is the result of photosynthesis or metabolic activity of organisms and biomass is basically solar energy stored in the chemical bonds of carbon and hydrogen. Breaking down and chemically modifying biomasses provides numerous pathways to synthetically produce renewable fuels to substitute today's fossil based carbon infrastructure. A major advantage of energy from biomass, despite other renewable energy technologies like e.g. solar power or wind energy is the transportability and storability of energy from biomass.

Biomass types are divided into 1st generation, 2nd generation and 3rd generation, where the use of 1st generation biomasses has been considered quite controversial in recent years. 1st generation biomasses include food crops like sugar and starch crops and are therefore competing with the food industry. For ethical reasons, first generation biomasses are not favourable for the use in energy or fuel production. More promising biomasses are 2nd and 3rd generation, where 2nd generation includes ligno-cellulosic biomasses (e.g. wood, straw and forest residues) and 3rd generation includes marine biomasses such as algae. Lignocellulose is a complex biomass subgroup which consists primarily of three principal components: Cellulose, hemicellulose and lignin. The relative amount of the three different compounds is highly biomass dependent, but generally the mass distribution is approximately 35-50 % cellulose, 20-35 % hemicellulose and 10-25 % lignin. The lignin fraction appears as a key compound with respect to inherent energy distribution [Publication C]. In biomass conversion to high density energy carriers, the elemental composition of biomass feedstock is of high interest. Table 1 shows the elemental composition and heating values of different lingo-cellulosic biomasses. The oxygen content is the major element in the biomass that is being removed through thermochemical conversion processes like hydrothermal liquefaction. The detailed composition of lingo-cellulosic biomass and reaction pathways during hydrothermal conversion is discussed in Publication C as a part of this thesis. The hydrogen to carbon ratio (H/C) and the oxygen to carbon ratio (O/C) change during hydrothermal liquefaction will be discussed in the following chapter.

Table 1: Ultimate analysis and heating values of different biomasses. Adapted from (7) and presented in Publication C

Biomass	HHV	C	H	N	S	Cl	O	Ash	H/C	O/C
Energy grass, Miscanthus	19.14	48.30	5.50	0.60	0.10	0.20	41.50	3.80	1.37	0.64
Energy grass, other	18.04	45.00	5.30	2.10	0.20	0.50	37.60	9.30	1.41	0.63
Wood material	19.58	49.00	5.70	0.40	0.10	0.10	41.90	2.90	1.40	0.64
Wood waste	18.47	49.70	6.00	1.70	0.00	0.10	41.00	1.50	1.45	0.62
Cereals	18.61	46.50	6.10	1.20	0.10	0.20	42.00	3.90	1.57	0.68
Millet	18.17	45.90	5.30	0.90	0.10	0.30	41.10	6.50	1.39	0.67
Sunflower	20.26	50.50	5.90	1.30	0.10	0.40	34.90	6.90	1.40	0.52
Hemp	18.04	45.70	6.30	0.60	0.00	0.10	44.10	3.20	1.65	0.72
Waste	15.97	42.60	5.70	3.40	0.40	0.10	32.20	15.50	1.61	0.57

Other plant, material	19.79	49.40	5.90	0.80	0.10	0.20	38.80	4.90	1.43	0.59
Other non-plant, material	20.32	49.30	6.70	1.20	0.20	0.20	37.80	4.60	1.63	0.58
All	18.87	47.60	5.80	1.20	0.10	0.20	39.50	5.60	1.46	0.62

1.2.1 Biomass Potential

Biomass, as a renewable energy source, can significantly participate in reducing world-wide CO_2 emissions. As mentioned above biomass is an abundant resource and is presently the largest renewable contributor in the energy sector, for the production of heat, electricity and fuels for transport (4) (3). Benefits of energetic use of biomass include reduction in greenhouse gas emission, improvements of energy security and trade balances, substituting fossil fuels with domestic biomass, forming opportunities for economic and social development in rural communities. Using waste and residues, further addresses waste disposal problems and the possibility of making better use of resources (8).

At present, forestry, agricultural and municipal residues, and wastes are the main feedstocks for the generation of electricity and heat from biomass. In addition, a very small share of sugar, grain, and vegetable oil crops are used as feedstocks for the production of liquid biofuels. (8)

According to the IEA Bioenergy report on sustainable and reliable energy sources, the current world biomass demand sums up to 50 EJ per year (compared to 553 EJ total energy consumption), whereas the estimated demand in 2050 will rise up to 50-250 EJ per year associated with a world-wide energy consumption of 600-100 EJ. When looking at biomass resources, the technical and sustainable potential has to be differentiated. 2050 Biomass technical potential: 50-1500 EJ/year, 2050 estimated world biomass demand: 50-250 EJ/year, 2050 Biomass sustainable potential: 200-500 EJ/year (8).

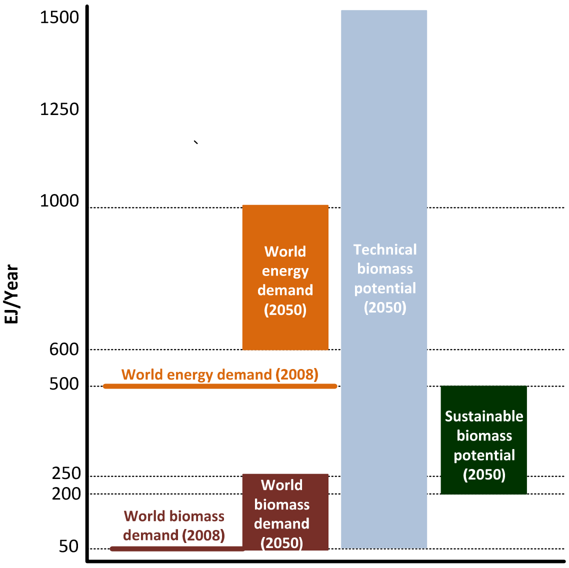


Figure 4: Sustainable vs. technical biomass potential, adapted from (8)

1.3 Potential of Advanced Fuels from Biomass

The general definition for advanced biofuels is biofuels from 2nd or 3rd generation biomass, specifically lignocellulosic biomass. Today most advanced biofuel technologies are in research and development (R&D), pilot and demonstration phase. The first commercial scale plants for advanced biofuels production are expected to be installed in the next decade, followed by a rapid growth of advanced biofuels after 2020. Pilot or demonstration plants are already operating in North America and the European Union. Today, biofuel production is equivalent to 175 million liters gasoline and by 2015 another 6 billion liters is being estimated by the International Energy Agency. After reaching commercialisation of advanced biofuels, they will eventually provide the major share of biofuel supply (5).

Biofuels will in the coming decades reduce dependency in fossil fuels and CO_2 emissions, of course demanding a sustainable process design and use of resources. Biofuels may reduce energy related CO_2 emissions by 2050 with 8% (~3.5 Gt CO_2-equivalent). (5)

Development of biofuels implementation in the EU is expedited by the Renewable Energy Directive 2009/28/EC. The directive established a European framework and set the goal to achieve a target of 20% share of renewable energy in the final energy consumption and a share of 10% of renewable fuels for the transport sector. Reaching those goals will contribute to reduction of emissions, improvement of fossil source independent energy supply accompanied by reduced energy import dependency. Important is to follow sustainability criteria of the directive.

Hydrothermal liquefaction is a promising pathway to drop-in advanced biofuels from biomass. Against other thermochemical conversion processes HTL delivers a fuel that can potentially be used directly as a marine fuel oil or further upgraded to diesel and aviation fuel by integrating the downstream upgrading process to existing conventional refineries.

Figure 5 shows prediction in the world-wide transport sector for 2050 and it is obvious that biofuel utilisation is increasing; from 2% biofuel share of world total transport in 2010 to 27% in 2050 (5). Main predicted application is the road passenger sector, but also marine and road freight transport form a major share.

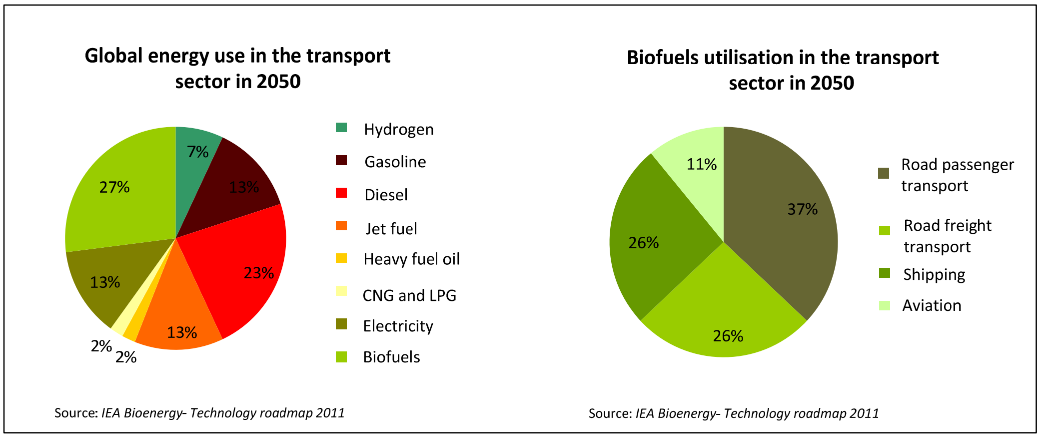
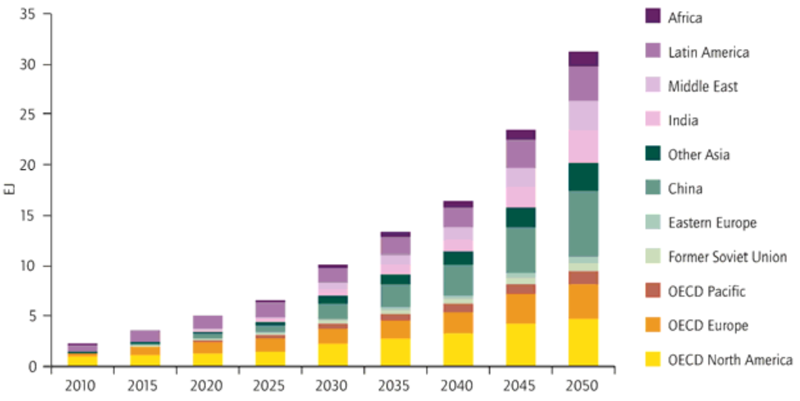


Figure 5: World energy supply by source and fuel demand for 2050, adapted from (5).

A major implementation barrier remains, however, even for advanced biofuels, and that is compatibility with existing fuels, hydrocarbon infrastructure and end user technologies. In order not to inhibit mobility, and to capitalize on the vast investments of knowledge and money into the hydrocarbon infrastructure, a further goal for advanced biofuels is that they should possess drop-in properties. The US based National Advanced Biofuel Consortium (NABC) defines drop-in fuels as hydrocarbon fuels from renewable sources, which meet all refinery and ASTM standards for any blending rate up to and including 100%, and which require no downstream technology modifications at end user level.



Note: FSU= Former Soviet Union.
Source: IEA, 2010c.

Figure 6: Biofuels demand by region 2010-2050 (5)

Figure 6 shows the world-wide trend in biofuel demand by region from 2010-2050. Over the next decade the highest demand is from non-OECD countries.

In this roadmap, biofuel demand over the next decade is expected to be highest in OECD countries, but non-OECD countries will account for 60% of global biofuel demand by 2030 and roughly 70% by 2050, with strongest demand projected in China, India and Latin America (Figure 6). Conventional biofuels are expected to play a role in ramping up production in many developing countries because the technology is less costly and less complex than for advanced biofuels.

Hydrothermal biomass conversion delivers a liquid high value hydrocarbon product. To reach the goal of delivering a drop –in advanced biofuel, detailed bio-crude characterisation has to be done, to determine potential upgrading strategies. Aim of this thesis work is to investigate upgrading strategies from crude HTL bio-oil to a sustainable advanced drop-in quality fuel. It includes standard characterisation of bio-crudes from pilot scale production and preliminary upgrading efforts. Figure 7 shows the schematic experimental procedure developed during the thesis. Part of the thesis is on process integration of an HTL plant to another renewable energy process.

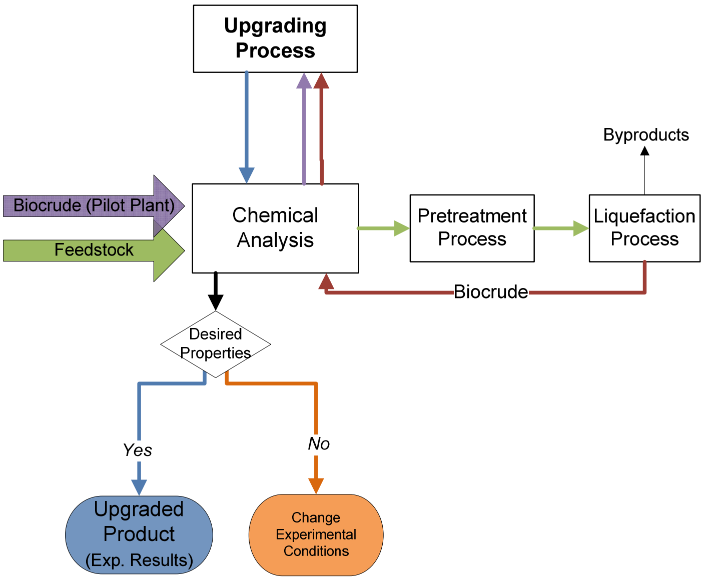


Figure 7: Schematic flow of experimental procedure

Chapter 2 Biomass to Advanced Drop-in Biofuel

This chapter will discuss the production, upgrading and application possibilities of bio-crude from hydrothermal liquefaction (HTL). It gives an introduction to standardized methods used for conventional fossil fuel, and discusses the implications of applying these to advanced biofuels in order to reduce upgrading costs, and identifying a pathway for biofuels to become economically viable.

2.1 Hydrothermal Conversion

Hydrothermal liquefaction (HTL) is a type of thermochemical conversion by which biomass feedstock is converted at temperatures from 280 to 450°C, pressures up to 35 MPa and residence times from 5 to 30 min, to a bio-crude with very high carbon conversion ratios, compare Figure 8. Water is a prerequisite for the process, making it especially suitable for wet biomasses such as sewage sludge, manure, wet agricultural residues etc., and even future feedstocks from marine sources such as algae. As residual streams often contain significant amounts of water, this relieves a drying step unlike gasification and pyrolysis. Thus, HTL offers a unique way of reclaiming water from energy processes. Adding dry biomasses to this or recycling water allows also widening the scope of input biomasses, including for example lignocellulosic biomasses and others. The product is a bio-crude that can be used as bunker fuel directly or upgraded to a drop-in standard refinery feedstock and subsequently to transportation fuel. Compared to conventional crude, bio-crude from HTL typically has higher heteroatom content depending on the biomass feedstock used. Detailed pathways during the conversion of lignocellulosic biomass are presented in Publication C.

Special properties of hot compressed water (HCW) are utilized to break down and restructure organic material through hydrothermal liquefaction, including hydrolysis, depolymerisation, defragmentation, dehydration and decarboxylation, obtaining long chained molecules, similar to alkanes in fossil crude oil, and with a very low oxygen and moisture content.

As mentioned above, the major role during HTL conversion plays the water and unlike other biomass conversion process biomass converted through HTL does not need drying, but can be directly converted into a bio-crude. Water at room temperature will not react with organic molecules; however during HTL liquefaction the water phase in the biomass slurry plays an important role and two physically properties of water change substantially during the heat up process; The dielectric constant ε_r, measurement for the relative permittivity decreases and the dissociation constant K_w of water increases intensely.

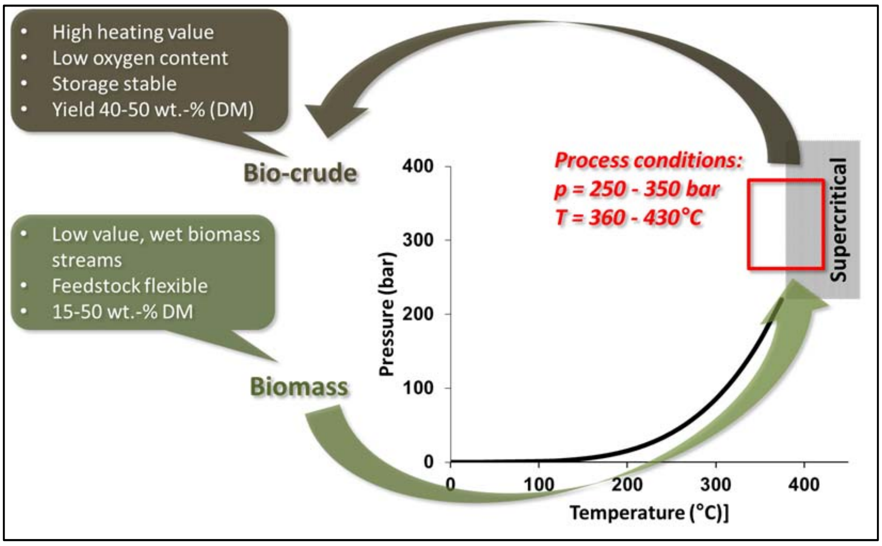


Figure 8: HTL in a phase diagram [Publication D]

The dielectric constant has an influence on the polarity of water. The constant decreases from 80.27 at 20°C to 11.36 at 360°C for saturated water (9). The water molecules relatively change from very polar to fairly nonpolar and the affinity to nonpolar organic hydrocarbons rises as well as their solubility in water. (10) This is due to a reduction of electronegativity of the oxygen molecule (less polar) in the water due to an increase in thermal energy and more evenly circulation of the shared electron of hydrogen and oxygen (10). The change in the permittivity leads to physical properties of water at 360°C even lower than acetone with ε_r = 20.7 at 25°C (11).

The dissociation constant Kw has an influence on hydrolysis reactions in the water phase. With an increase of temperature the Kw of the water increases. At atmospheric pressures and 25°C the K_w value is 10^{-14} compared to $10^{-11.62}$ at 300 bars and 360°C. An increase in the dissociation constant due to higher temperature, leads to an increase reaction rate of base- and acid catalysed reactions in water, far beyond natural acceleration (10). Both changes in properties of the water favour decomposition and repolymerisation reactions during HTL.

Figure 9 visualises literature studies on HTL and it shows the removal of oxygen from the biomass during HTL. The atomic hydrogen to carbon ratio (H/C) over the oxygen to carbon (O/C) of different biomass feedstock and the resulting HTL bio-crudes is shown.

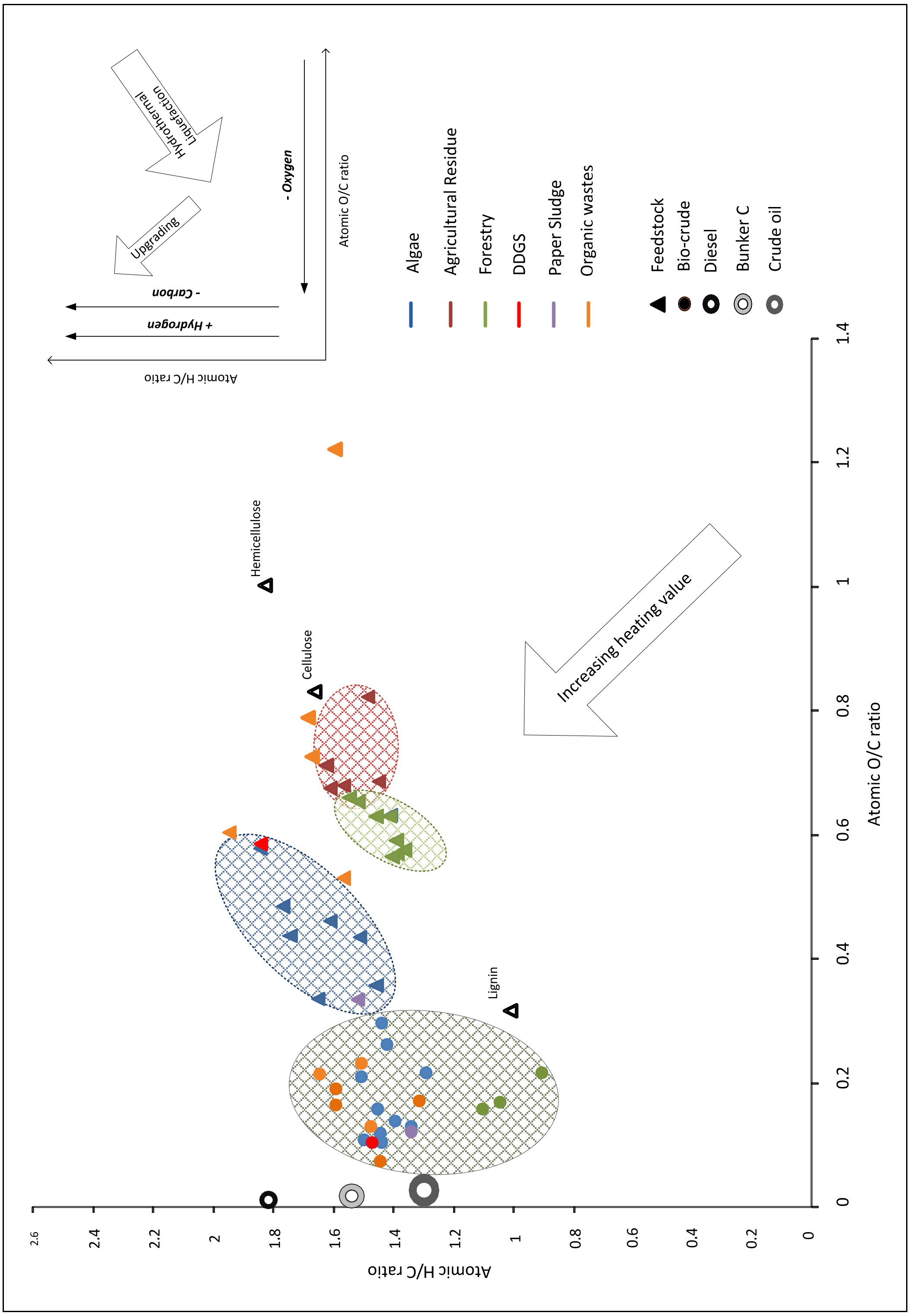


Figure 9: Van Krevelen Diagram of HTL conversion data from literature (12) (13) (14) (15) (16) (17) (18) (19) (20) (21) (22) (23) (24) (25) (26) (25) (27) (28) (29) (30) (31)

2.1.1 Continuous Bench Scale Unit

The Department of Energy Technology at Aalborg University commissioned a continuous bench scale pilot plant for the conversion of various biomass feedstocks through hydrothermal conversion.

The bio-crude has been produced during the commissioning of the continuous bench scale plant located at Aalborg University, Denmark. Designed and built by Steeper Energy, it is based on the Hydrofaction™ platform, and provides a versatile research platform to investigate continuous HTL under a wide range of process conditions and feedstocks. At pressures in the range of 250 up to 350 bar and reaction temperatures in the range 350 to 450 °C, wet biomass slurry is processed into a crude oil phase, a water phase containing soluble organics, a mineral and a gas phase.. Mechanically, the CBS1 plant has been designed for maximum operating pressures up to 400 bar and temperatures up to 550 °C, and a feed capacity in the ranges 5-30 kg per hour.

The plant consists of a feedstock preparation container, a control and utility system container and a process container. In the feedstock preparation container feedstock is milled and slurred with water and chemicals to produce pumpable slurry.

Figure 10: CBS #1 set-up at Aalborg University Campus, Denmark. Container in the front contains the pretreatment unit, the 2 containers in the back contain the process plant in the bottom and the control and utility system in the top.

The biomass slurry is pressurized by the pump system and heated by two induction heaters heat tracing installed in series. The feed is pressurized to 280 bars with a flow rate of 10-15 kg/h. The heated and partially converted slurry is fed to the reactors through a feed inlet in the top. In Reactor-1 and Reactor-2 the hydrothermal conversion is completed. The finished emulsified products, a slurry of water, oil, ash and synthesis gas, is subsequently cooled in Cooler 1, pressure reduced in the capillary pressure let-down system comprising small valve controllable tubes of a length of 4 - 500 m and diameter ranging from 1.4 – 2 mm, cooled to the desired product temperature in Cooler 2, degassed in the degasser and the remaining product including oil, water and minerals are collected in the product barrel for further separation.

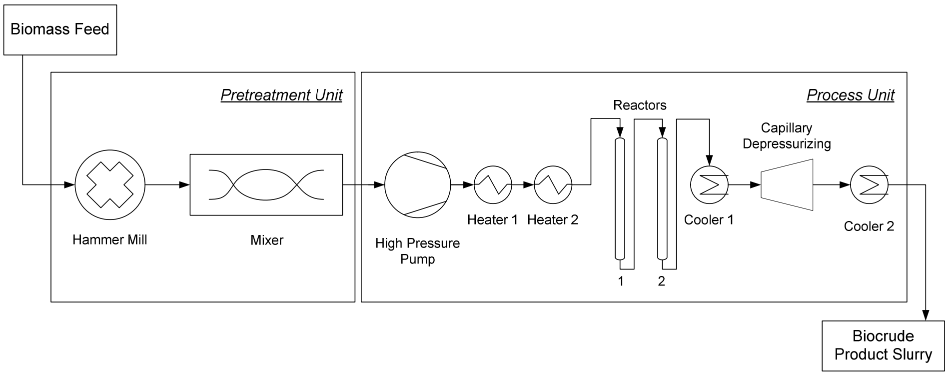


Figure 11: Schematic process flow of CBS #1

Figure 11 shows a schematic process flow diagram of the CBS1 unit. The biomass slurry is pressurized by the pump system and heated by two induction heaters installed in series. The heated and partially converted slurry is fed to the reactors through a feed inlet in the top. In Reactor-1 and Reactor-2 the hydrothermal conversion is completed. The finished emulsified products, a slurry of water, oil, ash and synthesis gas, is subsequently cooled in Cooler 1, pressure reduced in the capillary pressure let-down system comprising small tubes of varying length and diameter, cooled to the desired product temperature in Cooler 2, degassed in the in the degasser and the remaining product including oil, water and minerals are collected in the product barrel for further separation.

2.2 Crude Characterisation and Fuel Specification

To select adequate methods of processing heavy oils and residua, it is necessary to define the feedstock in as much detail as possible. However, the chemical composition of heavy oils and residua is more complex than that of light oils, and their precise chemical and physical constitution is not well understood. (32)

When processing crude feeds in refineries the crude composition and characterisation are of great importance for the design of a refinery. The transformation from crude to finished product requires detailed knowledge about the composition of the feed as well as the specifications of the finished, desired product. And the process will be designed depending on this fact. Characteristics are explained in the following paragraphs.

When looking for substitution of fossil crude oils, renewable fuels have to meet standard specifications and up-to date properties, to be integrated directly to the existing carbon infrastructure. Specifications are set by governmental policies and vary from country to country. It is desirable to characterise bio-crude similar to conventional crude, this way direct comparison is possible.

Standard test methods are being used for the specification of transportation fuels. The International Organization for Standardization (ISO) promotes worldwide proprietary, commercial and industrial standards, the American Society for testing and materials (ASTM) that develops and publishes voluntary consensus technical standards for a wide range of materials, products, systems, and services. In Europe the European Committee for Standardization (CEN) develops European Standards (EN) and is officially recognised as a European standards body.

Fuel specifications vary regarding their application. Jet fuel standards vary from diesel fuel standards. Advanced fuels from biomass have to meet those specifications and depending on the application more extensive or less extensive upgrading has to be applied to the bio-crude. In the following specifications of different fuels are being described.

2.2.1 Crude oil characterisation

Conventional crude oil is a complex mixture of hydrocarbon compounds, mainly hydrogen and carbon in varying proportions. Crude oil also contains organic impurities such as sulphur, oxygen, nitrogen and metals. The hydrogen to carbon ratio has a big influence on the physical properties of the crude oil; since conventional crude oil contains millions of different molecules, with a high number of non-repetitive isomers (33). As seen in Figure 12 crude oil can be divided into a variety of fractions, regarding they boiling point which correlates to the carbon chain length in the oil. Complete analysis of each single compound in the oil is virtually impossible. Therefore crude oils are normally characterised by standardized methods.

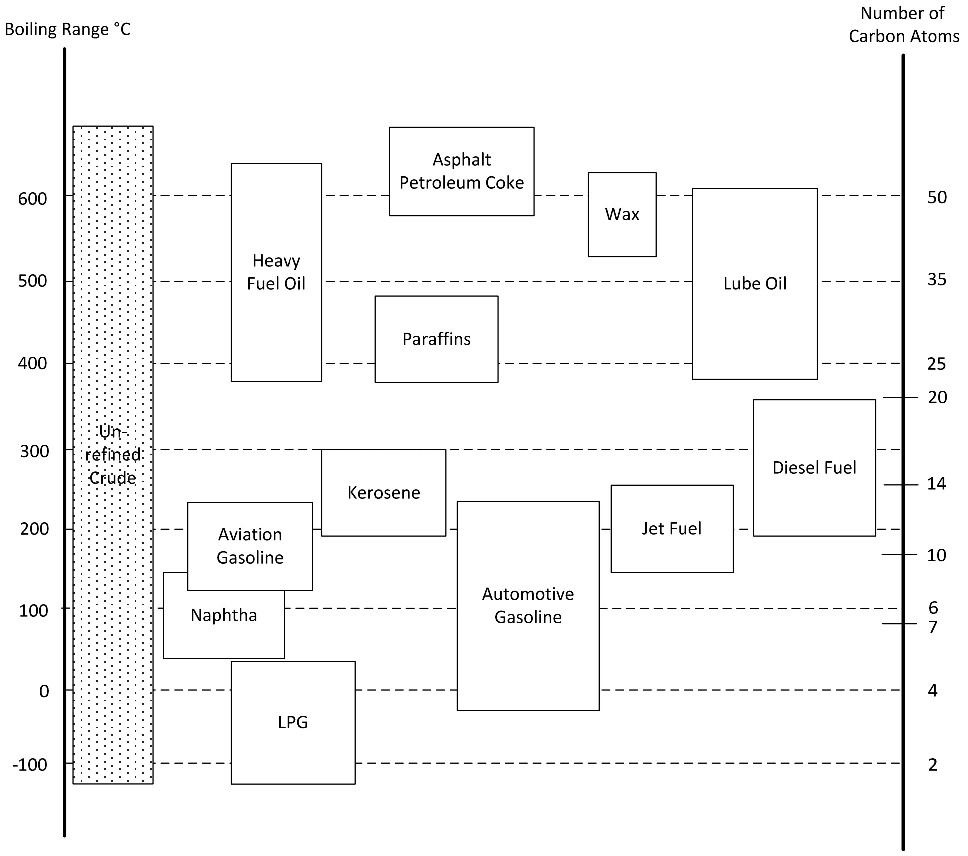


Figure 12: Principle petroleum products with carbon numbers and boiling ranges, adapted from (34)

Crude oils are generally characterised by an oil assay. An oil assay is specific for every crude oil and gives information about its physical and chemical properties. An oil assay is commonly used to estimate how much refractory and upgrading processes are needed to obtain marketable fractions of the oil. In the following properties included in an oil assay are described briefly.

API gravity

Crudes are divided into classes regarding their American Petroleum Institute (API) gravity. The API gravity relates to the quality of crude. The API gravity is a special function of relative density (specific gravity), calculated by the following:

$$API\ gravity, ° = \left(\frac{141.5}{specific\ gravity\ 15.56/15.56℃}\right) - 131.5 \qquad \text{Equation 1}$$

The lower the API gravity the heavier and of less quality is the crude. Extra heavy crudes or bitumen's have an upper limit of API gravity of 20°, heavy crudes have an upper limit of API gravity of 20 ° and a viscosity of 100cP. Intermediate crudes have an API gravity of 20°-30° whereas light oil has an API gravity above 30°.

Sulphur Content

Conventional crude oils have sulphur contents of 0.1 – 5 wt.-%. The quality of the crude is highly dependent on the amount sulphur in the oil. Environmental pollution in the form of sulphur oxides, corrosion of equipment and in the refined product, poisoning of catalyst can occur. Heavier fractions of crude oil contain higher amounts of sulphur.

Pour point

Pour point measurements give an idea of handling properties of the crude. As a rule of thum in refinery settings, it is known, that the higher the pour point the more parrafinic it is, the lower the more aromatic it is. The pour point is detected by measuring the flow properties of the crude at 3°C regarding ASTM standards.

Viscosity

Viscosity determination gives information about flow properties of the crude as well. And it stands also in correlation to parrafinicity and aromaticity of the crude. Generally the viscosity is determined at 2 temperatures (25 and 40°C) and can then be inter-or extrapolated using viscosity-temperature charts.

Distillation

Distillation of crude oil allows the separation into different boiling point fractions e.e. naphtha, light gas oil, heavy gas oil and residue. In laboratory scale Simulated Distillation can be done using a GC/MS.

Freezing point

The freezing point is of particular interest for aviation fuels, since it gives insight to the cold flow properties of a fuel. Aviation fuels have to work in high altitudes at low temperatures without plugging filters or nozzles.

Flash point

The flash point of a fuel reveals information about flammability and subsequently safety precautions that have to be taken into account for a specific fuel.

2.2.2 Crude oil and HTL bio-crude characterisation

To achieve the vision of advanced drop in biofuels, bio-crude from HTL as to meet common standards, therefore it is of big importance to investigate conventional crude oil properties versus bio-crude properties.

2.2.3 Jet fuel specification

Aviation turbine fuels can be divided in Jet A, Jet A-1 and Jet B fuels, according to U.S. ASTM standard D 1655 (35) and D 6615. The 3 classes are divided according to their freezing point which are -40°C, -47°C for Jet A and Jet A-1, respectively. Jet B is a so called wide-cut gasoline-containing grade and described in ASTM D 6615. Also several other countries issue jet fuel specifications; in most cases they are identical to the American counterparts.

Jet A is used as the general domestic jet fuel in the U.S. Half the world-wide domestic civil jet fuel consumption is covered by Jet A. For long-distance, high altitude, international flights and domestic flights outside the U.S. , Jet A-1 is being deployed. The use of Jet-B fuels is extremely limited. Since most airport fuel system designs are limited to one fuel grade, Jet A-1 is the most common and consumed fuel throughout the world.

When looking at the composition of jet fuels, jet fuels consist entirely of hydrocarbons and only trace amounts of sulphur or other approved additives are allowed. Jet fuels are generally produced from straight-run kerosene and hydrocracked streams. When looking at the specification requirements of jet fuels, they can be divided into two main groups; Bulk properties and trace properties. To change the bulk properties of a jet fuel significantly, major changes in the composition must have taken place. Bulk properties affect the availability of jet fuels strongly and make up for how much jet fuel can be produced from e.g. one barrel of oil. In Table 2 bulk properties and their limitations are listed. Trace properties can change about part per million and affect specific operating characteristics of the fuel. Trace properties include high temperature stability, storage stability, and corrosion, compatibility of the fuel with system materials, electrical conductivity, lubricity and contaminants in the fuel. Theses trace properties can be affected and controlled by additives. (22)

Table 2: Characteristic bulk properties of jet fuel, data found in (22)

Bulk Property	**Property**	**Purpose**	**Requirements jet fuel A-1 (35)**
Volaltility	Flash point, °C	Fire hazard estimations, Ignitability	> 38
	Distillation temperature, °C (with distillation recovery points at 10, 20, 50 and 90 %)	Ensure properly balanced fuel and engine combustion performance	10 % at < 205 Final boiling point <300
Fluidity	Freezing point, °C	Low temperature pumpability, filter plugging	< -47
	Viscosity (20°C), mm^2/s		< 8
Combustion	Smoke point, mm or	Burning quality (smoke formation, carbon deposition, and flame radiation)	> 25
	Naphthalene, vol.-%		< 3 (if smoke point >18)
	Net heat of combustion (lower heating value), MJ/kg		> 42.8
Emission	Total sulphur content, wt.-%	Sulphur oxide emission	< 0.3
Density	Density (15°C), kg/m^3	Fuel load calculations	775 to 840
Specific heat	Net heat of combustion (lower heating value)	Economics of engine performance	> 42.8
Aromatic content	Aromatics, vol.-%	Influences heat of combustion	< 25

2.2.4 Diesel and Bunker Fuel Specification

Diesel fuels of different kinds are used for land and marine transport. The boiling range of middle distillate fuels is 150-400°C. The most common used specification for diesel fuel is the ASTM D 975. Important properties are: volatility, fluidity, ignition quality, emission, density and stability.

Table 3: Properties of bunker and diesel fuel (36) (22)

Bulk Property	**Property**	**Purpose**	**Diesel ASTM**	**Diesel EN590**	**Bunker(RMK700) ISO**
Volaltility	Flash point, °C	Fire hazard estimations, Ignitability	38-52	55	60
	Distillation temperature, °C (with distillation recovery points at 10, 20, 50 and 90 %)	Ensure properly balanced fuel and engine combustion performance	90%recovery Max:288-338	95% recovery Max:370	-
Fluidity	Freezing point, °C		-	-	-
	Viscosity (20°C), mm^2/s		Max:2.4-4.1(40°C)	Max:4.5(40C)	700(50C)
Ignition quality	Smoke point, mm or	Burning quality (smoke formation, carbon deposition, and flame radiation)	-	-	-
	Naphthalene, vol.-%		-	-	-
	Net heat of combustion (lower heating value), MJ/kg		-	-	-
Emission	Total sulphur content, wt.-%	Sulphur oxide emission	Max:0.05-0.5	Max:0.2	4.5
Density	Density (15°C), kg/m^3	Fuel load calculations	-	Max:860	1010
Stability	**Net heat of combustion (lower heating value)**	Economics of engine performance	-	-	-
Aromatic content	Aromatics, vol.-%	Influences heat of combustion	35	-	-

Chapter 3 Upgrading

Regarding transportation fuels the Environment Protection Agencies (EPAs) world-wide set regulations to forbid or control the pollution of the environment.

The primary product from hydrothermal liquefaction, the bio-crude typically requires further upgrading before it obtains drop-in properties either at crude oil level, or as transport grade fuels. As a precursor to upgrading, it is essential to obtain detailed information on the composition of the bio-crude, in order to guide optimization of the process design towards a high yield of bio-fuels or other commercially relevant products. These characterisation methods have been presented in Chapter 2. schematically presents the decision making on how extensively the bio-crude has to be upgraded crucially depending on the application it is being used for. Bunker fuels have different characteristics compared to e.g. jet fuels, like discussed in section 2.2 and for some restriction HTL bio-crude shows the ability to even being applied directly and with little upgrading effort.

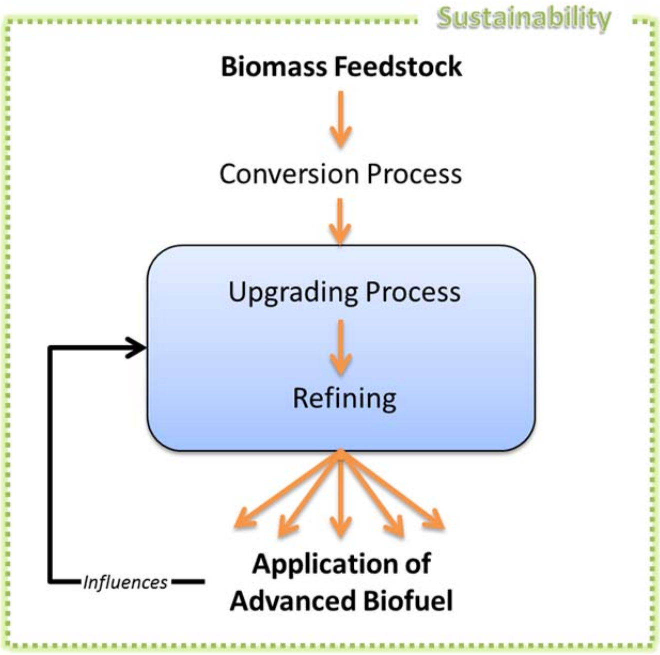


Figure 13: Biomass conversion process cascade

When considering upgrading of bio-crude it makes sense to look on upgrading methods in standard refinery setting. There heavy feeds are challenging and need more upgrading attention. And due to the rising attention heavy and problematic crudes get, recent advances in catalyst design and formulation have been made. For upgrading of bio-crudes the proper match of the feed with catalyst properties, reactor types and operating conditions has to be found.

In conventional refinery setting one process to improve crude oil properties is hydroconversion. Hydroconversion could be an option for the upgrading of HTL bio-crude as well, since it removes unwanted heteroatoms like sulphur, nitrogen and oxygen as well as metals and olefins and their unstable compounds (34). Hydroconversion can be divided into hydrotreating, hydrocracking and hydrogenation processes. Hydroconversion processes require hydrogen and a suitable catalyst (37). The process operating parameters used during hydroconversion, influences the reactions taking place. More severe conditions during the process (T> 360°C) lead to hydrocracking reactions.

Analytical methods for the characterisation of hydroconversion feeds need to be improved or developed to better predict the behaviour of catalysts and catalytic reactors when processing such feeds.

For bio-crude from hydrothermal conversion hydrocracking is not the favourable process to apply, since oxygen compounds in the feed will deactivated hydrocracking catalyst and oxygen in the feed can cause fouling of heat exchangers (38). Therefore hydrotreating as it is a less severe process has been chosen and preliminary upgrading on bio-crude from dried distillers grain (DDGS) feedstock has been done.

3.1 Hydrotreating

Research on upgrading of bio-crude from hydrothermal liquefaction have been conducted at the labs of CANMET Energy, Natural Resources Canada, Devon and are presented in Publication C of this thesis. Heteroatoms contained in the bio-crude can be removed during this process by the addition of hydrogen. Figure 14 shows the reaction taking place during heteroatom removal when hydroprocessing crude oil. During the process the atomic H/C ratio is increased and the heteroatom to carbon ratio is reduced at the same time. In literature upgrading research of bio-oils (pyrolysis) and bio-crude focuses on the removal of oxygen containing compounds so called hydrodeoxygenation reactions. Detailed chemical pathways and kinetic literature review on hydrodeoxygenation can be found in Publication B.

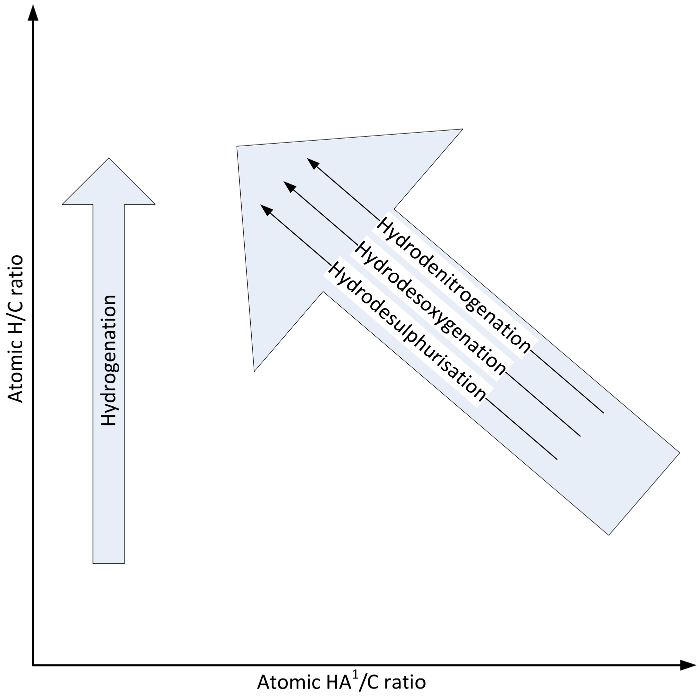


Figure 14: Hydrotreating pathways [1]: Heteroatom

3.2 Hydrotreating in Conventional Refineries

For hydroprocessing of bio-crude from HTL a suitable catalyst has to be found. For commercial hydrotreating of conventional refinery streams mainly CoMo and NiMo catalyst supported on gamma alumina (Al_2O_3) are being used. It has a high surface area, is stable at the temperatures used in hydroprocessing, and is relatively inexpensive (37).

Generally catalysts with an active phase of CoMo are more effective for HDS, whereas NiMo formulations have good activity for hydrogenation (HYD) and hydrodenitrogenation (HDN). However, if the nitrogen content in the feed is high, the NiMo catalyst would be preferred, since this formulation performs better the HDN reactions.

In refinery operation hydrotreating is often performed in multiple-bed systems. The first bed or catalyst layer is always designed to provide high HDM activity, the second is to provide some HDM but significant HDS, and the third is responsible for hydrocracking as well as HDS and HDN (39). Hereby the pore size and surface are of the catalyst plays an important role. Heavier fractions need larger pore sizes whereas lighter fraction need high surface are and therefore smaller pore sizes. The first bed or layer contains a large-pore catalyst, while in the second and third beds smaller pores and larger surface areas are required (40). Modern catalysts are optimised to have a high catalyst life span, stability, selectivity and activity when processing heavy feeds.

The activity of a catalyst is a major properties and research on hydrotreating of bio-crudes from HTL has to be done to find the optimal catalyst. Another issues when hydroprocessing heavy feeds, that is also important for bio-crude as feed, is the deactivation of the catalyst, due to nitrogen, oxygen, coke formation and metal deposition.

Heavy feedstocks as well as bio-crude from HTL (compare section 3.3) contain several metals, such as Ni, V, Fe, and so on, which in conventional crudes are present as porphyrins or chelating compounds. During hydrotreating these metals are transformed to sulphides (Ni_3S_2, V_3S_2, and V_3S_4) and deposit on the catalyst surface. These deposited transition metal sulphides cause a decrease in the number of catalytic sites, hinder the transport of reacting molecules to the internal catalyst surface, and eventually cause the complete plugging of the catalyst pores (37).

Nitrogen in the feed affects the poisoning of the acid side of the catalyst whereas coke formation blocks the catalyst pores. Metal deposition affects the life span of a hydroprocessing catalyst much more serious, since the deposition is not reversible as it is for coke by burning it off with oxygen. This means that the activity of a catalyst is highly dependent on the metal content in the feed.

In standard refinery setting a specific catalyst combination and reactor are being designed for each specific feed. For light feed usually the chemical composition of the catalyst and the surface are important, heavy feeds chemical composition and porosity of the catalyst are important to achieve optimum catalyst performance.

So, for light feeds, catalyst chemical composition and surface area are crucial, whereas chemical composition and porosity are more important in the case of heavy feeds. Although for both feeds the role of the support is important, in the latter case the support acidity and porosity have to be carefully designed to attain optimum catalyst performance.

Deactivation of the catalyst results in reduced catalyst stability or slow decrease in conversion over time. In refinery processing, when deactivation of the catalyst takes place, the temperature of the catalyst bed is increased gradually to steer the activity of the catalyst. Table 4 list hydroprocessing catalyst plugging, its causes and the practised solution in industry.

Table 4: Hydroprocessing catalyst bed plugging and its principal causes

Fouling	**Principal cause**	**Problem**	**Solutions**
Particulates	Contamination of feedstocks	Increased delta p Void fraction of the catalyst bed is being reduced Catalyst bed fully or partially plugged	Grading scheme Guard bed catalyst

Reactive molecules	Olefines and oxygenates	Carbon deposits Pore plugging	Increase in H_2 partial pressure Decrease in reaction temperature
Inorganic ions deposit	As, Ni, V, Fe, Ti, Si and so on	Pore plugging due to metal deposits Buried catalytic sites	Guard bed catalyst

Next to the choice of the catalyst the reactor set-up is also of great importance when designing a hydroprocessing unit for a specific feed. A variety of reactors exist. Fixed-bed reactors, moving-bed reactor and expanded- or ebbaluated bed reactor exist for hydrotreating. The operation in principal is similar but important parameters can differ, which are:

- Total pressure and hydrogen partial pressure
- Reaction temperature
- Hydrogen-to-oil ratio and recycle gas rate
- Space-velocity and fresh catalyst and feed rate

In general refinery operation the more impurities a feedstock has (heteroatoms, metals), the more severe process conditions have to be used (e.g. increasing hydrogen partial pressure, temperature, or H_2-to-oil ratio and decreasing space velocity) (37).

3.3 Upgrading Strategies for Bio-crude from HTL

Four different bio-crude samples from CBS1 are being characterised according to ASTM standards. At the time of submission of the thesis work, the assay has only been finished partly. The following will therefore be based on the data which was available at this, but the complete data sets and upgrading considerations will compiled into a manuscript based on this section. It is expected to be completed within the fourth quarter of 2013.

The bio-crude has been produced during the commissioning of the continuous bench scale plant located at Aalborg University, Denmark. Designed and built by Steeper Energy, it is based on the Hydrofaction™ platform, and provides a versatile research platform to investigate continuous HTL under a wide range of process conditions and feedstocks. At pressures in the range of 250 up to 350 bar and reaction temperatures in the range 350 to 450 °C, wet biomass slurry is processed into a crude oil phase, a water phase containing soluble organics, a mineral and a gas phase.. Mechanically the CBS1 plant has been designed for maximum operating pressures up to 400 bar and temperatures up to 550 °C, and a feed capacity in the ranges 5-30 kg per hour.

The plant consists of a feedstock preparation container, a control and utility system container and a process container compare Figure 2. In the feedstock preparation container feedstock is milled and slurred with water and chemicals to produce pumpable slurry.

The biomass slurry is pressurized by the pump system and heated by two induction heaters heat tracing installed in series. The feed is pressurized to 280 bars with a flow rate of 10-15 kg/h. The heated and partially converted slurry is fed to the reactors through a feed inlet in the top. In Reactor-1 and Reactor-2 the hydrothermal conversion is completed. The finished emulsified products, a slurry of water, oil, ash and synthesis gas, is subsequently cooled in Cooler 1, pressure reduced in the capillary pressure let-down system comprising small valve controllable tubes of a length of 4 - 500 m and diameter ranging from 1.4 – 2 mm, cooled to the desired product temperature in Cooler 2, degassed in the degasser and the remaining product including oil, water and minerals are collected in the product barrel for further separation.

Biomass Feedstock

Wood flour is used as a biomass feedstock for the conversion in the CBS unit. Tall oil is partly used to reach pumpability of the biomass slurry during processing and is in future intended to be replaced all the time with recycled bio-crude phase. The dry matter content of the biomass is 90 wt.-%. The water content of tall oil is 5 wt.-%. The biomass feedstock is prepared in the pre-treatment unit (shown Figure 7) of the CBS process plant. The wood flour is milled using a hammer mill to a particle size of approximately 0.5 mm and subsequently mixed with recycled water from previous runs, tall oil or bio-crude and homogenous K_2CO_3 catalyst.

The composition of the biomass slurry is shown in Table 5.

Table 5: Feedstock preparation details

	CBS 22	CBS 24	CBS 25	CBS 27
Wood flour (wt. -%)	13.2	18.7	12	16.1[1]
Catalyst (wt. -%)	2.2	2.0	1.7	2.0
Tall Oil (wt. -%)	18.1	-	32.3	11.7
Recycled bio-crude (wt. -%)	-	19.1	-	7.6
Water (wt. -%)	66.5	60.2	54	62.6
Water type	*Recycled*	*Recycled*	*Recycled*	*Recycled*
DM_{Feed} (wt.-%)	31.3	37.8	44.4	35.4

[1] Including bark flour with DM=44 wt.-%

Biocrude Product

The bio-crude slurry is separated from the water phase using a centrifuge. Subsequently the water and solids in the crude are separated by further centrifugation for 48 hours at 3800 rpm and 20 °C.

Biocrude Analysis

The analysis of the bio-crude has generally been completed according to ASTM standards for petroleum analysis, listed in Table 6.

Table 6: Analysis methods for bio-crude

Analysis	**Method**
Ultimate Analysis	
C,H,N	ASTM D 5291
Oxygen	Elemental oxygen analyser
Sulphur	ASTM D 4294
Water	ASTM D6304
Ash	ASTM D 482
Micro Carbon Residue	ASTM D 4530
Metal Content (Va,Ni)	ICP-MS
Solids	ASTM D4870
Total Acid Number	ASTM D 664
Density	ASTM D 4052
Viscosity	ASTM D 445 (40°C)
Pour Point	ASTM D 5949
Flash Point	ASTM D3828
Copper Corrosion	ASTM D130
Simulated Distillation	ASTM D7169

Results

Analysis on bio-crude from hydrothermal liquefaction has been done. The experimental results show promising

Conventional crude oils are divided into classes regarding their API gravity. The API gravity is a measurement of the lightness or heaviness of oils and is related to the density of the oil (41). Crudes can be divided into extra heavy crudes or bitumen (API gravity of ≤10°), heavy crudes (API gravity of ≤ 22.3˚), intermediate (API gravity of ≤31.1°) whereas light oil has an API gravity above 31.1°. Table 3 shows API gravities of crude oil of different qualities; Conventional extra heavy crude (Athabasca bitumen crude, Canada) (41), heavy crude (Maya crude, Mexico) (42), intermediate crude (Istmo crude, Mexico) (42) and light crude (Brent crude, UK) (43). Bio-crude from HTL before hydrotreating has an API of similar to extra heavy Athabasca bitumen oils.

High temperature simulated distillation has been conducted on the bio-crude feed CBS 22, 24, 25 and 27, respectively. The obtained distillation curves and yield of fractions have been compared to conventional crude oil distillation curves found in literature as shown in Figure 16.

Table 7: Fraction and API gravity of different crudes

Fraction Boiling range	API°	Naphtha IBP- 204°C	LGO 204°C-343°C	HGO 343°C - 524°C	Residue 524+°C
Bio-crude 22	11.4	17.58333	32.75	32.8795	16.78716
Bio-crude 24	16.8	11.60938	30.34715	36.27126	21.77222
Bio-crude 25	14.3	11.97333	26.61287	40.57977	34.51692
Bio-crude 27	17.4	16.41935	35.14065	20.83402	13.92308
Brent	38.1	33	24.8	25.3	16.9
Istmo	26.9	24.1	24.8	28.6	22.4
Maya	21.67	15.2	16.6	24.7	43.4
Athabasca	5.9	3.1	17.1	22.6	57.2

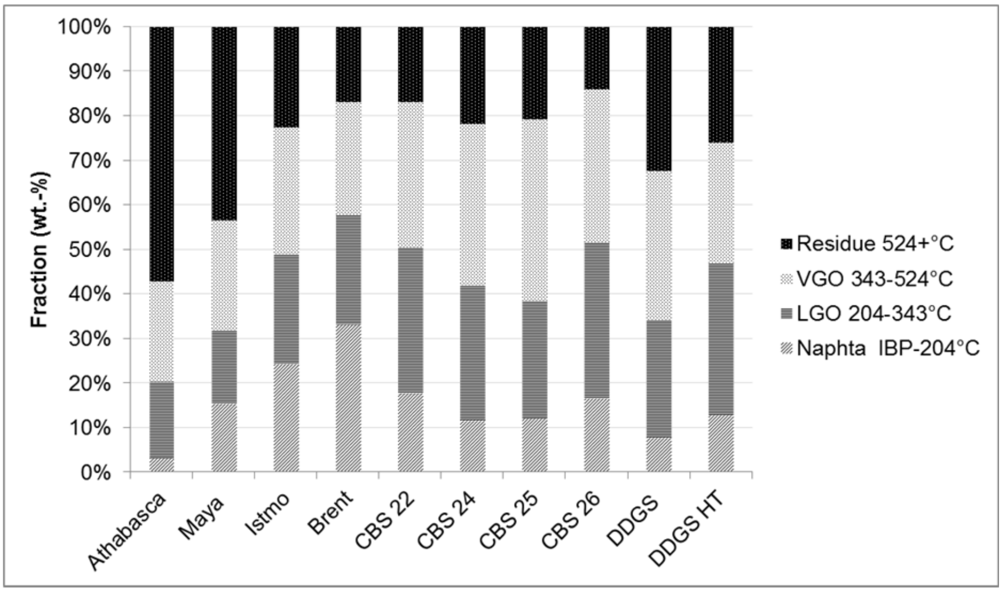


Figure 15: Comparison of fraction yield, for CBS bio-crude 22-27 and DDGS bio-crude from publication C

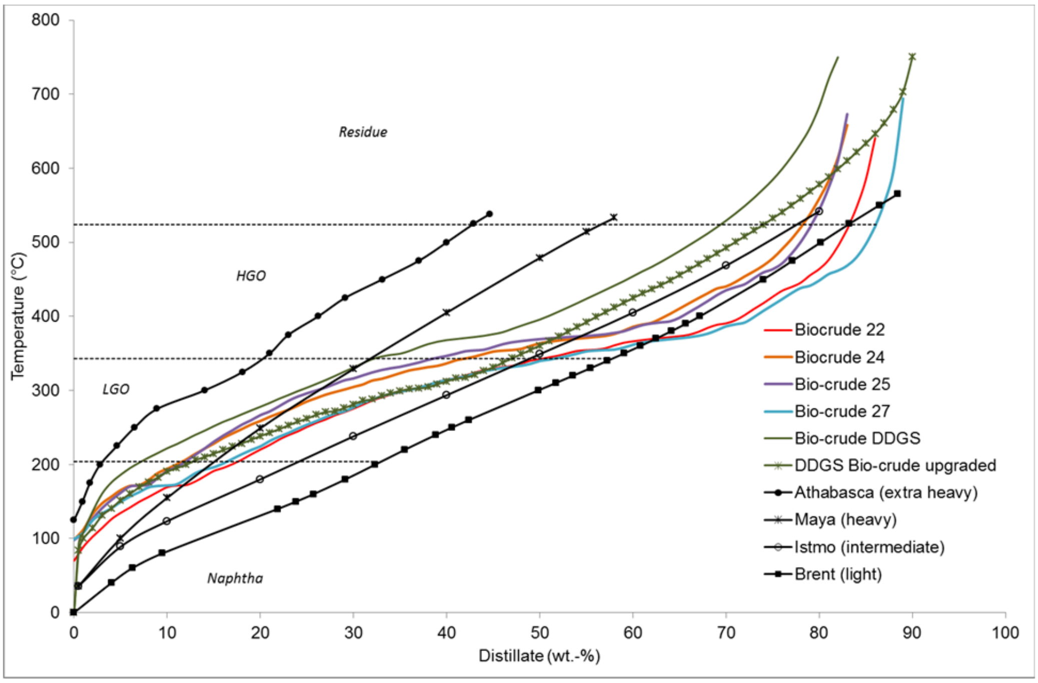


Figure 16: Comparison of HTL Bio-crude with conventional crudes of different qualities

Elemental analysis, simulated distillation and density have been measured for all raw CBS bio-crudes as. The density of the bio-crudes ranges from 0.95 g/ml to 0.99 g/ml. Conventional crude oil entering a refinery normally has an oxygen content of maximum 1.5 wt.-%, sulphur content of <6.0% and Nitrogen contents of <2 wt.-%, compare Table 8. The elemental analysis of the crudes was not available at submission of the thesis. Table 8 shows results of the analysis and includes data for conventional crude entering a standard refinery.

Table 8: Analysis results of bio-crude feed and conventional crude

	CBS 22	CBS 24	CBS 25	CBS 27	Conventional Crude (44)
Density at 15.6 °C (g/ml)[a]	0.954	0.9899	0.9706	0.9504	0.75-1
API° Gravity	11.4	16.8	14.3	17.4	5-50
Solids (wt.-%)	<0.01	<0.01	<0.01	<0.01	-
Carbon Residue (wt.-%)					-
Ash (wt.-%)	0.499	0.208	0.354	0.069	-
Water Content (wt.-%)	1.11	0.96	0.91	0.4	<3 (45)
Kinematic Viscosity (cSt)					7.29[a]
40°C	15	44.56	36.94	11.97	
TAN (mgKOH/g)	43.46	41.26	59.60	36.78	<1-
Metals (ppm)					
Ni	5.8	3.3	7.7	3.3	
V	<6.6	<6.6	<6.6	<6.6	<1000
K	3743	1170	1790	37.4	
Fe	122.6	190.4	278.9	269.8	
Flash Point (°C)	15	37	39	39	
Pour Point (°C)	-9	0	0	-12	-46 [a]
Ultimate	n/a	n/a	n/a	n/a	
C (wt.-%)	n/a	n/a	n/a	n/a	83.0 - 87.0
H (wt.-%)	n/a	n/a	n/a	n/a	10.0 - 14.0
N (wt.-%)	n/a	n/a	n/a	n/a	0.1 - 2.0
S (wt.-%)	n/a	n/a	n/a	n/a	0.05 - 6.0
O (wt.-%)[e]	n/a	n/a	n/a	n/a	0.05 - 1.5
Heating value [MJ kg^{-1}]			40.88±0.01 (HHV)		43.05±1.4[b] (LHV)

a Mesa Crude Oil

b Calculated using Boie correlation (46)

c Dry and ash free

d Dry

e Calculated by difference

Chapter 4 Sustainability and Process Integration

This chapter deals with the approach of realising a sustainable biomass to biofuel process. Sustainability is a function of social, economic and environmental factors – generally summarized by the 3P approach: People, Planet and Profit. Issues associated with sustainability should ultimately be addressed at all three levels, but in this context, focus is on feedstock and process sustainability.

4.1 Sustainable Advanced Drop-in Biofuels

Because biomass will also be a prime feedstock for a wide range of chemical, nutritional and pharmaceutical products, like shown in the biomass pyramid in Figure 2, it will become a limited, high-cost commodity. Therefore, for liquid biofuels to be produced in bulk, it is necessary to identify eligible low-value organic streams such as animal manure, agro-industrial waste and sewage sludge.

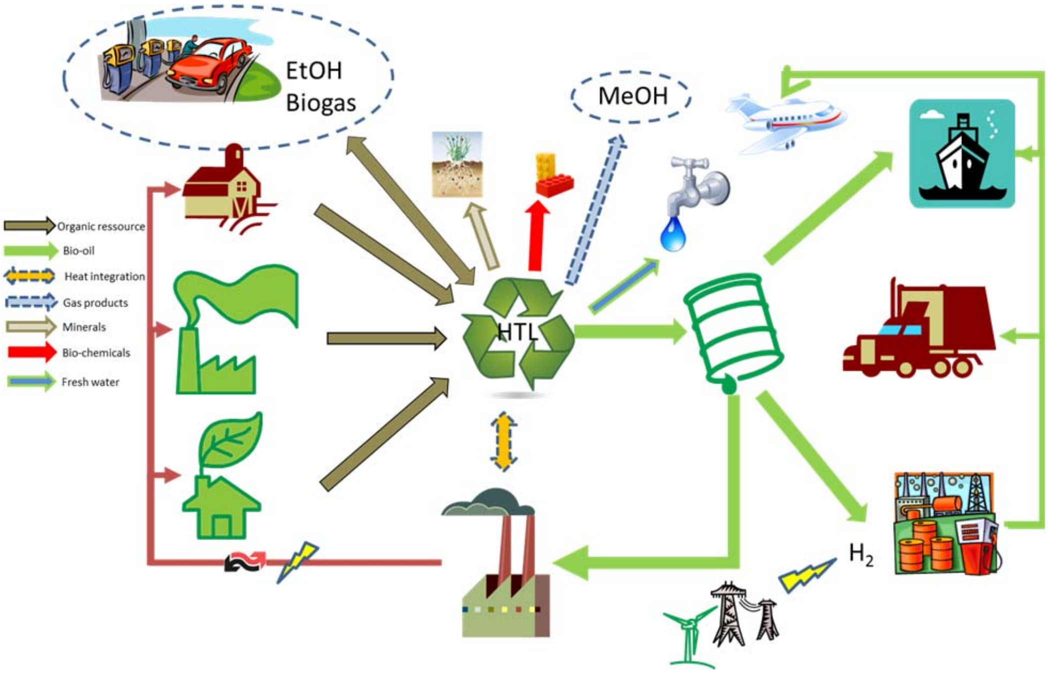


Figure 17 A closed system integrating waste and drop-in product streams with an HTL process.

For this to occur, the identification of suitable combinations of feedstocks and conversion processes that ensure high process and conversion efficiency and the sustainability of the biomass in the fuel conversion process are critical. The latter is especially important because the energy from fossil fuels used during the biomass conversion process has to be considered in the carbon footprint. The responsible use of resources and minimisation of fossil energy inputs to the process should be targeted. Only an efficient and sustainable process will be commercially compatible and have the capacity to endure. Appropriate process integration and optimisation are the best methods to achieve this.

4.2 Integrated HTL Plant

When considering the necessity of upgrading HTL bio-crude using hydroconversion process a sustainable hydrogen source has to be found. Additionally the biomass to drop-in fuel process needs to be as energy and conversion efficient as possible. It is obvious that the process energy needs have to be as low as possible to achieve an efficient and sustainable process, and for this reason, internal heat integration plays an important role in plant design, as well as does heat and mass integration across system boundaries. This can be realised by integrating the conversion process to other renewable processes or, as indicated in Figure 18, by integrating the upgrading step with the primary conversion step. In such a process optimization strategy, for example, hydrogen from the gas phase produced by HTL could be recycled to the upgrading process, possibly supplementing an external supply of hydrogen from renewable sources such as wind electricity driven water hydrolysis. A prerequisite for this type of process integration is of course detailed knowledge of the bio-crude produced in the primary conversion step, in order to determine minimum upgrading requirements to bring it to drop-in level, and to determine the most optimal process layout for this.

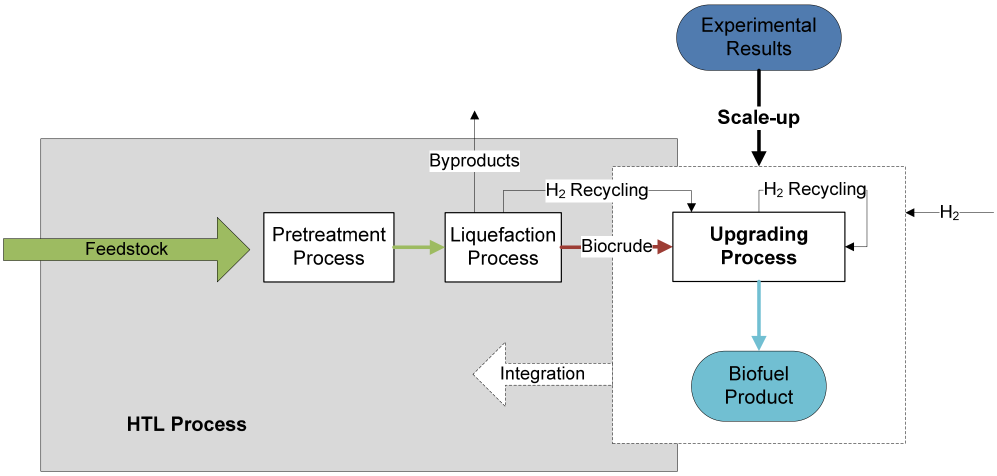


Figure 18: Integration of HTL and initial upgrading step through process integration.

4.2.1 Modelling of an integrated HTL-Biogas plant

In Publication A the concept of an integrated hydrothermal liquefaction process with two way synergies is presented. Within the general framework of Figure 17, the presented process design integrates a biochemical (biogas plant) and a thermochemical (hydrothermal liquefaction) biomass conversion process, with the HTL feeds resulting from the waste stream of the biogas plant. The end-products of the integrated process are a range of biofuels (biogas, biocrude or upgraded biofuel) that can be used for transportation as well as for combined heat and power (CHP) production. The idea is to obtain hydrogen needed for the upgrading of the HTL bio-crude from steam reforming of the biogas product from the biogas plant. Biogas that is not used for the production of hydrogen as well as hydrogen off-streams are used to cover the plants energy needs. A schematic mass-flow is shown in Figure 19.

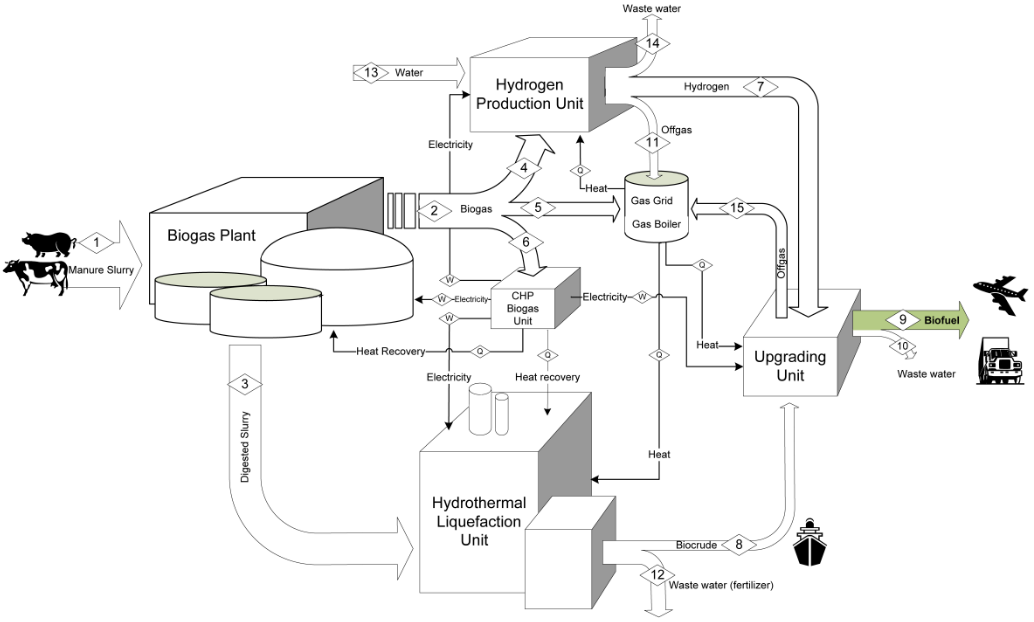


Figure 19: Integrated HTL/Biogas plant (Publication A)

In Aspen Plus a model has been developed to investigate material- and energy balances when integrating those two processes. Modelling of biomass feeds and HTL bio-crude properties is rather challenging and Aspen does not offer build-in features for this. Due to that the biomass input slurry has been modelled as non-conventional compounds, using ultimate and proximate analysis of the feedstock stream. This way of defining the stream uses Aspen default models that predict the density, specific heat capacity and the heat of formation as a function of temperature etc. The models that require the proximate and ultimate analysis are defined to fit coal-derived or char-like materials. Proximate and ultimate analyses for this study have been found in literature.

Another important issue when modelling biomass conversion processes in Aspen is the property method chosen. On the basis of the selected property method, Aspen evaluates thermodynamic properties of the different compounds, and inaccuracies in this respect will have significant impact on modelling results. A graduate study carried out at Aalborg University (47) clearly illustrates this for properties of water near the critical point, and supports the choice of the SRK equation of state used in Publication A as the most accurate property method for feedstocks with high water content. Combined with the higher heat capacity of the water phase relative to that of the other components of the feedstock mix, the importance of being able to accurately model density and specific heat capacity of the water dominates model accuracy. Regarding on which property method being used, Aspen evaluates thermodynamic properties of the different compounds. Results of the study can be found in Publication A.

Chapter 5 Summary

The results from the characterisation of bio-crude from the CBS pilot plant look very promising. With probably hundreds or thousands of compounds of components in the bio-crude, detailed characterisation of each single molecule seems unrealistic and a way has to be found to obtain sufficient information on the bio-crude to evaluate the crude quality without years spent in the lab. The idea has been to use existing standards and by this, comply with biofuel drop-in criteria at the same time. This allows existing hydrocarbon infrastructure to be used, as well as existing refinery structure and chemical and technical knowledge. The effort in characterisation and process understanding and integration has been the major outcome of this thesis and guides a path to design efficient and commercially attractive upgrading strategies for advanced biofuels. During this thesis work five bio-crude assays have been developed, according to ASTM standards. Preliminary upgrading results from bio-crude from dried distiller grain (DDGS) have been reported, providing initial results on which to build upgrading of future oils from a range of sustainable feedstocks. Furthermore in regard to sustainability, it has been made essential to find a way of supplying sustainable hydrogen sources and ways of integrating a HTL process to make it highly efficient and commercially attractive, have been discussed in this work.

References

1. **BP.** *BP Statistical Review of World Energy 2013.* 2013.

2. **IEO.** *International Energy Outlook.* s.l. : Administration, U.S. Energy Information, 2010.

3. **OECD/IEA.** *World Energy Outlook 2012.* s.l. : OECD/IEA, 2012.

4. *International Energy Outlook 2013.* Washington, DC : U.S. Energy Information Administration, 2013.

5. **International, Energy Agency.** *Technology Roadmap - Biofuels for Transport.* Paris : OECD/IEA, 2011.

6. **EU Commision.** *Renewable energy progress report.* Brussels : European Commission, 2013.

7. *Prediction of heating values of biomass fuel from elemental composition .* **Friedl, A., et al., et al.** 2005, Anal Chim Acta, Vol. 544, pp. 191-8.

8. **IEA.** *BIOENERGY – A sustainable and reliable energy source.* s.l. : IEA Bioenergy, 2009.

9. *Dielektrizitätskonstante und Ionenprodukt von Wasser und Wasserdampf.* **Grigull, U.** 6, 1983, Brennstoff-Wärme-Kraft, Vol. 35.

10. **H.P. Blaschek, T. Ezeji, J. Scheffran.** Biofuels from Agricultural Wastes and Byproducts. [auteur du livre] Y.Zhang. *Chapter 10 - Hydrothermal Liquefaction to Convert Biomass into Crude Oil.* s.l. : Wiley-Blackwell, 2010.

11. *Dielectric Constants of Water, Methanol, Ethanol,Butanol and Acetone: Measurement and Computational Study.* **M. Mohsen-Nia, H. Amiri, B. Jazi.** 2010, Solution Chemistry, Vol. 39, pp. 701–708.

12. *Hydrothermal liquefaction of dried distillers grains with solubles: a reaction temperature study.* **A. J. Mørup, P. R. Christensen, D. F.Aarup, L. Dithmer, M. Aref Hasen Mamakhel, M. Glasius, B. Brummerstedt Iversen.** 2012, Energy&Fuels, Vol. 26, pp. 5944-5953.

13. *'Hydrothermal liquefaction of the brown macro-alga Laminaria saccharina: effect of reaction conditions on product distribution and composition.* **Anastastasaki K., Ross A.B.** 7, 2011, Bioresource Technology, Vol. 102, pp. 4876-83.

14. *Thermochemical conversion of swine manure: an alternative process for waste treatment and renewable energy production.* **B. J. He, Y. Zhang, T. L. Funk, G. L. Riskowski, Y. Yin.** 6, 2001, Transactions of the ASAE , Vol. 43, pp. 1827-1833.

15. *Thermochemical conversion of biomass to liquid products in the aqueous medium.* **Demirbas, A.** 2005, Energy Sources, Vol. 27, pp. 1235-1243.

16. *Hydrothermal Liquefaction of Macroalgae Enteromorpha prolifera to Bio-oil.* **Dong Zhou, Liang Zhang, Shicheng Zhang.** 2010, Energy Fuels , Vol. 24, pp. 4054-4061.

17. *Hydrothermal processing of swine manure into oil using a continuous reactor system: development and testing.* **K. S. Ocfemia, Y. Zhang , T. Funk.** 2, 2006, Transactions of the ASABE, Vol. 49, pp. 533-541.

18. *Hydrothermal processing of swine manure to oil using a continuous reactor system: effects of operating parameters on oil yiled and quality.* **K. S. Ocfemia, Y. Zhang, T. Funk.** 6, 2006, Transactions of the ASABE, Vol. 49, pp. 1897-1904.

19. *Production of heavy oils with high caloric values by direct liquefaction of woody biomass in sub/near-critical water.* **Lad, C. Xu and N.** 2008, Energy & Fuels, Vol. 22, pp. 635–642.

20. *Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content.* **P. Biller, A.B. Ross.** 2011, Bioresource Technology, Vol. 102, pp. 215-225.

21. *Nutrientrecycling of aqueous phase for microalgae cultivation from the hydrothermal liquefaction proces.* **P. Biller, A.B. Ross, S.C. Skill, A. Lea-Langton, B. Balasundaram, C. Hall, R. Riley, C.A. Llewellyn.** 2012, Algal Research, Vol. 1, pp. 70-76.

22. **Rand, S. J.** *Signifiance of test for Petroleum Products.* Bridgeport : ASTM International, 2003.

23. *Subcritical hydrothermal liquefaction of cattle manure to bio-oil: Effects of conversion parameters on bio-oil yield and characterization of bio-oil.* **Sudong Yin, Ryan Dolan, Matt Harris, Zhongchao Tan.** 2010, Bioresource Technology, Vol. 101, pp. 3657–3664.

24. *Oil production from garbage by thermochemical liquefaction.* **T. Minowa, M. Murakami, Y. Dote, T. Ogi and S.-Y. Yokoyama.** 2, 1995, Biomass and Bioenergy , Vol. 8, pp. 117-120.

25. *'Chemical properties of biocrude oil from the hydrothermal liquefaction of Spirulina algae, swine manure, and digested anaerobic sludge.* **Vardon DR, Sharma BK, Scott J, Yu G,Wang Z, Schideman L, Zhang Y, Strathmann TJ.** 7, 2011, Bioresource Technology, Vol. 102, pp. 8295-8303.

26. *Comparative Evaluation of Thermochemical Liquefaction and Pyrolysis for Bio-Oil Production from Microalgae.* **U. Jena, K. C. Das.** 2011, Energy Fuels, Vol. 25, pp. 5472-5482.

27. *Comparative studies of products obtained at different temperatures during strawliquefaction by hot compressedwater.* **X. Z. Yuan, J. Y. Tong, G. M. Zeng, H. Li, W. Xie.** 2009, Energy & Fuels, Vol. 23, pp. 3262–3267.

28. *'Experimental study on the direct liquefaction of Cunninghamia lanceolata in water.* **Y. Qu, X. Wei, C. Zhong.** 2003, Energy, Vol. 28, pp. 597–606.

29. *Prediction of higher heating values of biomass from proximate and ultimate.* **Yin, Chun-Yang.** 2011, Fuel, Vol. 90, pp. 1128-1132.

30. *Recovery of liquid fuel from hydrocarbon-rich microalgae by thermochemical liquefaction .* **Yutaka Dote, Shigeki Sawayama.** 12, 1994, Fuel, Vol. 73, pp. 1855-1857.

31. *Production and characterization of bio-oil from hydrothermal liquefaction.* **Zou Shuping, Wu Yulong, et al., et al.** 2010, Energy, Vol. 35, pp. 5406-5411.

32. **Ancheyta, Jorge et Speight, James G.** *Hydroprocessing of heavy oils and residua.* Boca Raton, FL : Taylor & Francis Group, LLC, 2007.

33. **Wiehe, I. A.** *Process Chemistry of Petroleum Macromolecules.* Boca Raton, FL : CRC Press, Taylor&Francis Group, 2008.

34. **Fahim, M., Al-Sahhaf, T. et Elkilani, A.** *Fundamentals of Petroleum Refining.* s.l. : Elsevier, 2010.

35. **ASTM Standard, D1655.** *Standard Specification for Aviation Turbine Fuels.* West Conshohocken, PA : ASTM International, 2013.

36. **ISO.** *8217:2012.* s.l. : International Organization fo Standards, 2012.

37. **Speight, James G.** *Heavy oil and extra heavy oil upgrading.* s.l. : Elsevier, 2013.

38. **Parkash, A. S.** *Refining Processes Handbook.* Burlington : Elsevier, 2003.

39. *Selection of catalysts and reactors for hydroprocessing.* **Furimsky, E.** 2, 1998, Applied Catalysis A: General, Vol. 171, pp. 177–206.

40. *Major Scientific and Technical Challenges about Development of New Processes in Refining and Petrochemistry.* **Decroocq, D.** 5, 1997, Oil & Gas Science and Technology, Vol. 52, pp. 469-489.

41. **Speight, James G.** *The Chemistry and Technology of Petroleum.* s.l. : CRC Press, 2010.

42. *Simulated Distillation Yield Curves in Heavy Crude Oils: A Comparison of Precision between ASTM D-5307 and ASTM D-2892 Physical Distillation.* **Espinosa-Peña, Marcela, Figueroa-Gómez, Yolanda et Jiménez-Cruz, Federico.** 6, 2004, Energy Fuels, Vol. 18 , pp. 1832–1840.

43. [En ligne] TOTSA TOTAL OIL TRADING SA, 2006. http://www.totsa.com/pub/crude/index2.php?&iback=3&rub=11&expand=3&image=europe#.

44. **Speight, James G.** *Refinery of the future.* Oxford : Elsevier, 2011.

45. **Wauquier, Jean-Pierre.** *Petroleum Refining: Crude oil, petroleum products, process flowsheets, Volume 1.* Paris : Editions Technip, 1995.

46. **Boie, W.** *Vom Brennstoff zum Rauchgas.* Leipzig : Verlagsgesellschaft Leipzig, 1957.

47. **TEPE2-803, Group.** *Hydrothermal Liquefaction of black liquor .* Aalborg : Aalborg University, 2013.

48. *Continuous production of bio-oil by catalytic liquefaction from wet distiller's grain with solubles (WDGS) from bio-ethanol production.* **Toor, Saqib Sohail, et al., et al.** 2012, Biomass and Bioenergy, Vol. 36, pp. 327-332.

49. *Liquid fuel production from sewage sludge by catalytic conversion using sodium carbonate.* **S. Yokoyama, A. Suzuki, M. Murakamit, T.Ogi, K. Koguchi and E. Nakamura.** 1987, Fuel, Vol. 66, pp. 1150-1155.

50. *A review of recent advances on process technologies for upgrading of heavy oils and residua.* **Rana, M.S., Samano, V., Ancheyta, J., Diaz, J.A.I.c.** 9, 2007, Fuels, Vol. 86, pp. 1216-1231.

51. **Speight, James G.** *Refinery of the future.* Oxford : Elsevier, 2011.

52. **Speight, James G.** *The chemistry and technology of petroleum processes.* New York, NY : Marcel Dekker Inc., CRC Press, 1999.