

Mestrado Integrado em Engenharia Química

Biomass to Liquid Biofuels Processes

Tese de Mestrado

desenvolvida no âmbito da disciplina de

Projecto de Desenvolvimento em Ambiente Empresarial

Diana Raquel Bastos da Fonseca



Departamento de Engenharia Química

Orientador na FEUP: Prof. Doutor José Carlos Lopes

Orientador na empresa: Dr. Vítor Verdelho Vieira

Julho de 2008

Biomass to Liquid Biofuels Processes

Diana Raquel Bastos da Fonseca



July 31, 2008



*Pelo sonho é que vamos,
Um passo em frente a cada dia.
Chegamos? Não chegamos?
Haja ou não haja frutos,
Pelo sonho é que vamos...*

*Basta a fé naquilo que temos!
Basta a esperança
Naquilo que talvez não teremos...
Basta empenhar a alma
Com a mesma alegria
Naquilo que desconhecemos...*

*Chegamos? Não chegamos?
Mas pelo sonho é que vamos...*

Ivo Freitas, 2001

Agradecimentos

Ao Dr. Vítor Verdelho, que me proporcionou esta oportunidade e se manteve sempre presente em apoio e orientação, agradeço os conselhos, a preocupação, a orientação, a amizade.

Ao Professor Doutor José Carlos Lopes, meu orientador na FEUP, pelo apoio e orientação. À Professora Doutora Madalena Dias pelo apoio, e principalmente pela preocupação pessoal e profissional.

À Dra. Susana Pinheiro agradeço pela incansável energia para me motivar, orientar, corrigir e sobretudo apoiar nos momentos de hesitação, mas também pela grande amizade e enorme simpatia. À Dra. Joana Flores e Dra. Margarida Rossi pela enorme simpatia, e por estarem sempre preocupadas em apoiar!

Aos meus pais e maninha pela motivação, pelo carinho, pela energia, por estarem sempre presentes quando preciso deles, pela força, por abdicarem muitas vezes da sua felicidade em prol da minha, pelos conselhos, pelo apoio que sempre se revelou indispensável na minha vida... por tudo o que não consigo exprimir em palavras!

Ao meu namorado, Nuno, pela paciência nos momentos mais difíceis, pela compreensão, pelos conselhos, pelo encorajamento, pelo carinho ... por seres o meu porto de abrigo!

À Bé, à Elodie, ao Gaspar e à Joantina (minha colega de jornada - curta mas intensa!), pela ajuda, pelo ombro amigo, pela paciência nos meus desabafos e devaneios, e especialmente pela força... por estarem sempre presentes quando preciso de vocês!

Ao Eng^o Nuno Coelho e Dr. João Navalho pela simpatia, interesse e preocupação em fazerem-nos “sentir em casa”! À Dra. Vanessa Geraldes pela enorme hospitalidade e amizade, mas também por partilhar com muita paciência o seu trabalho. À Eng^a Victória Del Pino pela hospitalidade, pelo interesse e apoio, e especialmente pela simpatia e animação. À Doutora Teresa Lamela pela dedicada partilha de conhecimentos e pela amabilidade. A todos os colaboradores da Necton pela simpatia e hospitalidade.

A todos aqueles, familiares e amigos, que de uma forma ou de outra contribuíram para a realização deste trabalho.

A todos, Muito Obrigada!

Abstract

In a near term future biofuels will be needed to displace petroleum derived fuels, which are reaching unimaginable prices. Besides that, oil deposits are largely concentrated among a small number of countries, conceding them a virtual monopoly of this market. This situation destabilizes the energy security system in countries like Portugal, which largely depends on petroleum energy sources. To accurately plan a strategy for biofuels production it is necessary to fully understand the currently available options for biofuels production, which can be achieved with a detailed flow diagram on biomass conversion processes. That's the centrepiece of this work, which brings together a *Biomass Conversion Map*. Presently

New 2nd generation biofuels do not threaten the food prices and security of supply as 1st generation biofuels did, and there is already a confirmation that they have lower GHG - GreenHouse Gases - emissions than petroleum based fuels. The main barrier now is proving their energetic and economic viability in a commercial scale. Most of the biomass conversion processes have already moved from the lab-scale to pilot plants. Many researchers presented economic estimates on 2nd generation biofuel prices, and the majority compensates the petroleum based fuels prices.

However, since biofuels technology is an area of active research, new technologies are continually being developed and novel processes are likely to emerge in the future. To fulfil the *Biomass Conversion Map* an extensive literature search was conducted, but further improvements are constantly made. A bibliometric study indicates that lignocellulosic fermentation and gasification for subsequent biofuels production are the technologies that present a higher increase in research number. It was performed a biorefinery concept, that tries to represent what could be a near term biorefinery for microalgae main feed, optimized for liquid biofuels and high-value co-products production.

The microalgae may be converted into a diesel type fuel after the oil extraction, or converted to HTU-oil. A diesel type fuel production may be preferred if the microalgae has high oil content. The conversion of this oil into biodiesel may be achieved through transesterification or by hydrotreatment producing a synthetic diesel. However the hydrotreatment process seems to be the most promising.

The future biomass conversion technologies future may pass through genetically modify microalgae to better solar energy conversion. The conversion most promising conversion route may be hydrotreatment to produce green diesel, HTU-oil production or bio-oil production through flash pyrolysis, oils that can be further used directly in fuel engines, or can be incorporated as feed for conventional refineries, and that allow the production of a diesel type fuel with properties very similar to the conventional diesel.

Keywords:

biofuels, biomass, microalgae, biotechnology, biorefinery

Sumário

Num futuro próximo, prevê-se que os biocombustíveis passem a ser fundamentais como forma de substituir os combustíveis fósseis, que atingem actualmente preços impensáveis. Outro factor determinante é a posse de todas as grandes reservas de petróleo estarem num pequeno nicho de países, que dessa forma ganham o monopólio neste mercado. Esta situação ameaça a segurança energética de muitos países como é o caso de Portugal, que são fortemente dependentes da energia de origem fóssil. Para por em prática uma estratégia viável na produção de biocombustíveis, é necessário um vasto conhecimento das opções disponíveis e das suas recentes alterações. Isso pode ser conseguido através de um diagrama de fluxo actualizado, descrevendo as interacções entre os vários tipos de biomassa, processos de conversão e consequentes biocombustíveis produzidos. Essa é a peça central deste trabalho, denominada *Biomass Conversion Map* (secção 3.3).

A 2ª geração de biocombustíveis, ao contrário dos de 1ª geração, não ameaçam a segurança económica e de fornecimento dos produtos alimentares. Além disso, a grande maioria destes biocombustíveis têm menores emissões de gases de efeito de estufa do que os combustíveis fósseis (secção 3.4). O grande desafio actualmente é tornar estes biocombustíveis viáveis numa escala comercial, embora a maioria dos processos utilizados para produzir estes biocombustíveis já tenham passado da escala laboratorial para fases piloto (secção 3.6). Muito investigadores têm publicado estimativas dos preços, a curto e longo prazo, dos biocombustíveis de 2ª geração (secção 3.5). Um estudo da evolução anual do número de artigos publicados para cada tecnologia foi realizado na secção 3.6, indicando que a conversão de lignocelulose por fermentação e o processo de gasificação são as tecnologias que apresentam uma maior taxa de aumento do número de pesquisas. O desenvolvimento de um modelo de biorefinaria, em que a principal fonte de alimentação são as algas (secção 3.8), teria enormes vantagens no maior aproveitamento de todos os recursos materiais e energéticos disponíveis.

As microalgas podem ser convertidas num combustível similar ao gasóleo convencional após extracção do óleo microalgal, ou convertidas em petróleo sintético através do processo *HTU*. O primeiro caso pode ser preferível se a microalga possuir uma grande quantidade de óleo. A conversão deste óleo pode ser realizada através de transesterificação produzindo biodiesel, ou através de *hydrotreatment* (hidrogenação e isomerização), cujo produto final é um gasóleo sintético, muito similar ao gasóleo convencional. Dentro destes dois processos, o *hydrotreatment* apresenta-se mais promissor.

O futuro dos biocombustíveis poderá passar pela utilização de microalgas geneticamente modificadas, para aumentar a sua eficiência na captura da luz solar. Os processos de conversão mais promissores são o *hydrotreatment* para a produção de gasóleo sintético, e o *HTU* e *flash pyrolysis*, que produzem um bio-crude capaz de ser incorporado nos motores a combustão, ou que podem ser utilizados como alimentação às actuais refinarias.

Contents

1	Introduction.....	1
1.1	Framework and Project Presentation.....	7
1.2	Work Contributions	7
1.3	Thesis Organization.....	8
2	State of the Art.....	9
3	Technical Description and Discussion of Results.....	11
3.1	Biomass types: inputs identification	11
3.2	Biomass conversion system	15
3.3	Evaluation of the Biomass Conversion Processes	16
3.3.1	Identification of Inputs and Outputs of the Technology	16
3.3.2	The <i>Biomass Conversion Map</i>	18
3.4	Biofuels Overview.....	20
	Pure vegetable oil	20
	Biodiesel	20
	Bioethanol.....	20
	ETBE	21
	Biobutanol	21
	Bio-oil	21
	HTU-oil and HTU-diesel	21
	Biomethanol.....	22
	DME	22
	Synthesis gas.....	22
	Green Diesel and Green Gasoline	22
	Biogas and Methane.....	22
3.5	Economic Assessment	23
3.5.1	Technology associated costs	23

3.5.2	Biofuels final prices.....	26
3.6	Technology Progress Trends	27
3.6.1	State of Technology and main progress trends	27
3.6.2	Bibliometric Patterns.....	32
3.7	Case-study: Microalgae Fuels	33
3.7.1	Biomass Characterization.....	33
3.7.2	Technical Evaluation of the Technology	34
3.8	Biorefinery	37
3.8.1	Microalgae based biorefinery flow diagram	38
4	Conclusions	40
5	Evaluation of the Performed Work	42
5.1	Achieved Goals	42
5.2	Other Works Completed	42
5.3	Limitations and Future Work	42
6	References.....	43
<i>Appendix 1</i>	<i>Processes description</i>	<i>47</i>
1.1	Fermentation routes and Lignin Upgrading.....	48
1.2	Gasification and Pyrolysis routes	52
1.3	Oil crops and wet biomass conversion	55
<i>Appendix 2</i>	<i>GHG emissions and energy balance.....</i>	<i>59</i>
<i>Appendix 3</i>	<i>Economic data</i>	<i>60</i>
3.1	Economic studies of the technologies.....	60
3.2	Studies on biofuels prices comparison.....	62
<i>Appendix 4</i>	<i>Development trends data.....</i>	<i>66</i>
<i>Appendix 5</i>	<i>Bibliometric data.....</i>	<i>69</i>
<i>Appendix 6</i>	<i>Microalgal biomass composition data</i>	<i>72</i>

Notation and Glossary

Biogas	Biological gas (from anaerobic digestion)
BLG	Black Liquor Gasification
BTL	Biomass-To-Liquid
CBP	Consolidated Bio-Processing
CHP	Combined Heat and Power (co-generation)
CLC	Catalytic Low temperature Conversion
CNG	Compressed Natural Gas
DME	Di methyl ether
EC	Commission of the European Communities
ECN	Energy research Centre of the Netherlands
EEA	European Environment Agency
EECA	Energy Efficiency and Conservation Authority
EP	European Patent Office
ETBE	Ethyl tertiary butyl ether
EtOH	Ethanol
EU	European Union
FCC	Fluid Catalytic Cracking
FT	Fischer-Tropsch
GEO	Genetically Engineered Organism
GH ₂	Gaseous hydrogen
GHG	GreenHouse Gas(es)
GMO	Genetically Modified Organism
GTL	gas-to-liquid
HDO	Hydro-deoxygenation
HTU	hydro-thermal upgrading
IEA	International Energy Agency
ISP	Incentive Savings Plan
JAPIO	Japan Patent Information Organization
LNG	Liquefied Natural Gas
MOGD	Methanol to Olefins, Gasoline and Diesel
MTBE	Methyl tertiary butyl ether
MTG	Methanol to Gasoline
NG	natural gas
NREL	National Renewable Energy Laboratory
O&M	Operations and Maintenance
PCT	Patent Cooperation Treaty
PDU	Process Developing Unit
PM	Particular matter

PVO	Pure Vegetable Oil
RES-E	Electricity from Renewable Energy Sources
RME	Rapeseed methyl ether
SME	Soybean methyl ether
SNG	Synthetic Natural Gas
SSCF	Simultaneous Saccharification and Co-Fermentation
SSF	Simultaneous Saccharification and Fermentation
SWG	Supercritical Water Gasification
Syngas	Synthesis Gas (mixture of CO and H ₂)
UNEP	United Nations Environment Programme
USPTO	United States Patent and Trademark Office
WGS	Water Gas Shift
WTI	West Texas Intermediate (type of crude oil)

1 Introduction

One of the greatest problems that many industrialized countries as Portugal have been facing, is the great dependency upon energy imports and in particular on oil imports. As a matter of fact Portugal imports almost 85 % of his total energy demand. As can be observed in figure 1, in this total demand almost 60 % corresponds to fossil fuels (Rosa, 2006).

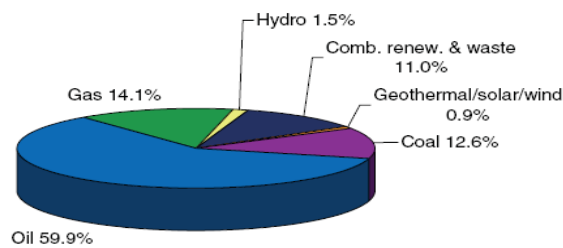


Figure 1 - Share of total primary Energy supply in Portugal, 2005 [source: IEA Energy Statistics] (International Energy Agency)

Recently, a new climbing on the oil prices reaching unimaginable values has occurred (figure 2). This climb is being originated by the international juncture, by the instability in the producer countries and most recently by the new and growing demand in emerging countries like China and India. In July the value was already 130 US\$ the oil barrel.



Figure 2 - Recent climb in oil prices (WTI Nymex: blue, ICE Brent: black) [source: IEA Energy Statistics]

Other two major energy challenges, beyond security of supply, are sustainability and climate change, since industrialized countries are also a large emitter of greenhouse gases (GHG), which contribute to global warming. In fact, European Union (EU) CO₂ emissions are forecast to rise by approximately 5% by 2030 (Larsen et al., 2003). In terms of GHG there is now scientific, social and political recognition that they are responsible for the changes on our climate.

This growing energy concerns combined are increasing the interest in bioenergy, especially biofuels. According to Exxon Mobil 2007 (figure 3), biofuels contribution growth for world energy consumption is estimated at 7.6 % for 2030. As transport, especially road transport, is a main oil consuming and GHG-generating sector in the EU, securing and diversifying the energy supply for transport in an environmentally-friendly way is a key transport, energy and environmental policy objective for the EU (Kavalov & Peteves, 2005). In addition they are an integral part of the emerging “bio-economy”, where plant material is used to produce specific chemicals and bulk industrial chemicals.

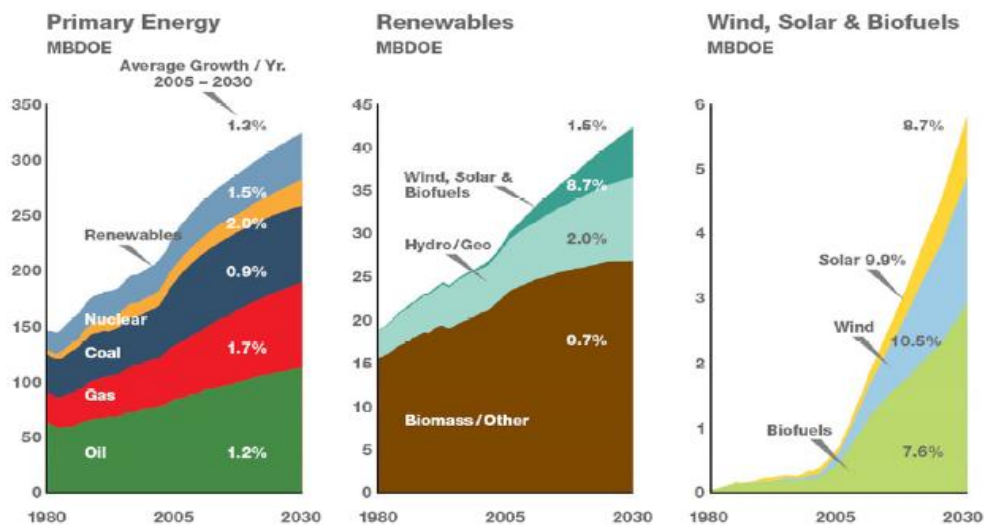


Figure 3. Estimations of relative contributions and expectations for the growth of various energy sources (Nylund et al., 2008).

These concerns had also led the Council of the EU to recently agree that Europe should develop a sustainable and integrated climate and energy policy. One of the most important agreements related with GHG emissions is the Kyoto Protocol, which Portugal is compromised to fulfil. In figure 4 are represented the Portuguese targets as well as the projections for 2010 and the Kyoto targets for 2012.

"The Kyoto Protocol is an agreement under which industrialized countries will reduce their collective emissions of *greenhouse gases* by 5.2 % compared to the year 1990 (but note that, compared to the emissions levels that would be expected by 2010 without the Protocol, this limitation represents a 29 % cut). The goal is to lower overall emissions of six greenhouse gases - *carbon dioxide* (CO₂), methane (CH₄), *nitrous oxide* (N₂O), *sulphur hexafluoride* (SF₆), *hydrofluorocarbons*, and *perfluorocarbons* - averaged over the period of 2008-2012. National limitations range from 8 % reductions for the EU and some others to 7 % for the US, 6 % for Japan, 0 % for Russia, and permitted increases of 8 % for Australia and 10 % for Iceland" [Source: press release from the United Nations Environment Program (UNEP)].

EU MEMBER STATE	2003	2004	2005	PROJECTIONS 2010	KYOTO TARGET 2012	% UNDER KYOTO TARGET	
ESTONIA	21.2	21.2	20.7	18.9	40		52.7%
LATVIA	10.7	10.7	10.9	13.6	23.3		41.6%
BULGARIA	-	68.9	69.8	87.1	127.3		31.6%
ROMANIA	-	160.1	153.7	192.5	259.9		26.0%
LITHUANIA	16.7	21.1	22.6	33.5	44.1		24.0%
HUNGARY	83.3	79.5	80.5	87.4	114.9		23.9%
POLAND	382.5	396.7	399	420	551.7		23.9%
CZECH REPUBLIC	147.5	147.1	145.6	145.7	180.6		19.3%
SLOVAKIA	51.1	49.5	48.7	58.3	67.2		13.2%
UNITED KINGDOM	658	660.4	657.4	595.6	678.3		12.2%
SWEDEN	70.9	69.7	67	69.8	75.2		7.2%
GERMANY	1024.4	1025	1001.5	955.4	972.9		1.8%
% OVER KYOTO TARGET							
LUXEMBOURG	11.3	12.8	12.7	14.2	9.1		56.0%
AUSTRIA	92.5	91.2	93.3	92.5	68.7		34.7%
SPAIN	407.4	425.2	440.6	410.2	331.6		23.7%
ITALY	577.3	580.5	582.2	587.3	485.7		20.9%
FINLAND	85.4	81.2	69.3	85	71.1		19.5%
SLOVENIA	19.7	19.9	20.3	21.6	18.6		16.1%
DENMARK	73.6	68.2	63.9	62.6	54.8		14.2%
PORTUGAL	83.7	84.6	85.5	88	77.4		13.7%
IRELAND	68.4	68.6	69.9	68.4	63		8.6%
GREECE	137.2	137.6	139.2	150.4	139.6		7.7%
NETHERLANDS	215.4	218.4	212.1	211.8	200.4		5.7%
BELGIUM	147.6	147.6	143.8	141.6	135.9		4.2%
FRANCE	560.9	556.1	553.4	569	564		0.9%
MALTA	3.1	3.2	3.4	2.2	NO TARGET		
CYPRUS	9.2	9.9	9.9	12.2	NO TARGET		

Figure 4. Kyoto CO₂ emission targets. The 2010 projection figures are based on existing domestic policies and measures, already implemented by the member states. Values are in Megaton of CO₂ equivalents (Mt CO₂-eq) [Source: EEA, based on EU Member States greenhouse gas inventories; November 2006]

The progression of emission standards for diesel cars and gasoline cars, in terms of nitrates (NO_x) and particulate matter (PM), are represented on figure 5.

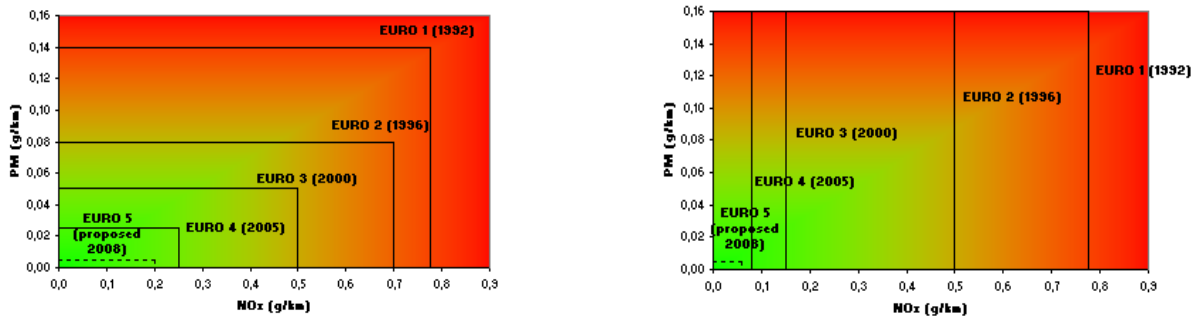


Figure 5. Simplified chart showing the progression of European NO_x and PM emission standards for Diesel cars (left) and Gasoline cars (right) [source: European Emission Standards]. Note: For Petrol cars, until Euro 5 there were no PM limits

The European Commission considers biofuels as a major feasible alternative to contribute to these policy goals in the near to medium term [COM (2001) 547]. So, one of the key goals of the EU’s energy and environment policy is to promote the utilization of renewable energy sources in order to reduce greenhouse gas emissions to meet the commitments of the Kyoto Protocol and to improve the security of fuel supply.

The EU Commission has taken several steps to promote the utilization of renewable energy resources in different sectors. The main directives are RES-E (Electricity from Renewable Energy Sources), biofuels for transport, combined heat and power, emission trading and landfill directive which have at least indicative targets for 2010 in Europe.

The RES-E target to be achieved by Portugal in 2010 is 39 % of gross electricity consumption. However Portugal has been moving further away from its RES-E target between 1997 and 2004. In part, this is due to the fact that the target is not entirely realistic, since it was based on the exceptional hydropower performance of 1997. As a consequence, Portugal is not expected to reach its target, even if measures are successful.

Target shares of biofuel penetration in the transport fuel market in the EU have been therefore set up - 2 % by the end of 2005 and 5.75 % by the end of 2010 of all petrol and diesel, on energy content basis, for transport purposes [Directive 2003/30/EC]. The Portuguese targets are represented on table 1.

Table 1 - Targets for the substitution of fossil fuels for renewable fuels, according to Directive 2003/30/EU (Rosa, 2006)

Year	Biofuels	Natural gas	Hydrogen	Total
2005	2	-	-	2
2010	5,75	2	-	7,75
2015	7	5	2	14
2020	8	10	5	23

Since January 2006, when Directive 2003/30/EC was transposed into national law, the following types of support are available for biofuel production: total or partial exemption from excise duty up to a quota that is annually set, and total ISP exemption for biofuels produced in certain pilot projects.

The conversion of biomass to energy (also called bioenergy) encompasses a wide range of different types and sources of biomass, conversion options, end-use applications and infrastructure requirements.

According to a study presented on *Biomass & Bioenergy Conference 2008* entitled “Environmental Aspects of the Biofuels for Transport in Europe” (Jungmeier, 2008) currently there are about 40 combinations of raw material, conversion process and respective biofuel produced under discussion.

Biomass can be converted into useful forms of energy using a number of different processes. Factors that influence the choice of conversion process are: the type and quantity of biomass feedstock; the desired form of the energy, i.e. end-use requirements; environmental standards; economic conditions;

and project specific factors. In many situations it is the form in which the energy is required that determines the process route, followed by the available types and quantities of biomass.

Biomass can contribute in stabilizing CO₂ concentrations in the atmosphere in two ways: through biomass production for fossil fuel substitution and through CO₂ storage in vegetation and soil. Biomass resources include wood and wood wastes, agricultural crops and their waste by-products, municipal solid waste, animal wastes, waste from food processing, and aquatic plants and microalgae (Balat, 2008).

Besides its potential to be carbon-neutral if produced sustainably, modern bioenergy shows the promise of covering a considerable part of the world’s energy needs, increasing the security of energy supply through the use of indigenous resources, and improving local employment. The trend towards bioenergy has been further encouraged by technological advances in biomass conversion and significant changes in energy markets (Larsen et al., 2003).

Biofuels - liquid, solid or gas fuel for transport produced from biomass (according to the Directive 2003/30/EU), have the potential to address two items: they appear to be carbon-neutral because the carbon they emit to the atmosphere when burned is offset by the carbon that plants absorb from the atmosphere in his growth, and renewable because fresh supplies can be grown as needed (The Royal Society, Jan 2008). The carbon cycle is represented in figure 6.

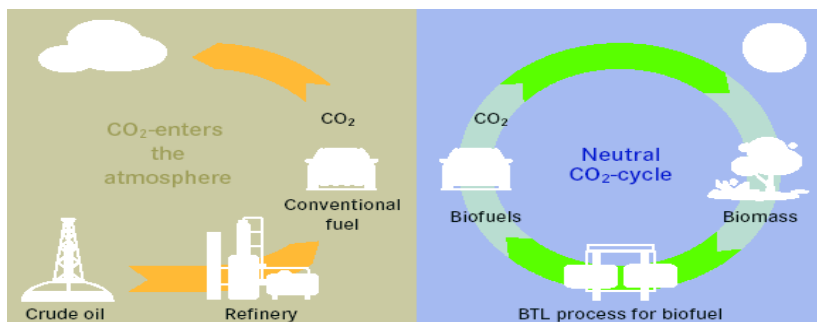


Figure 6. Broken (fossil fuels) and closed (biomass) carbon/CO₂ cycle [source: (Kavalov & Peteves, 2005)]

The advantage of producing a liquid fuel from biomass is the lower transportation costs when the fuel is not used at the production site, but it needs to be stored and transported. Liquid fuels are cheapest and easiest to transport, as they have the largest energy density. Solid fuels are easy and safe to transport, but can be more expensive, as they have lower energy density. Gaseous fuels are expensive, difficult and more dangerous to transport, these should be used at the production site.

The biofuels considered in the Directive 2003/30/CE include a variety of products, among which: bioethanol, biodiesel, biogas, biomethanol, bio-DME (dimethyl ether), bio-MTBE (methyl tertiary butyl

ether), bio-ETBE (Ethyl tert-butyl ether), synthetic biofuels, biohydrogen and pure vegetable oil (PVO). However, with respect to liquid biofuels for transport vehicles, the most common are biodiesel, bioethanol or its derivative ETBE. These can be commercialized in its pure form or in fossil fuels blending. (Rosa, 2006)

First generation biofuels are already being used in commercial quantities, notably for transport (Ruiz, 2005). These are biofuels made from sugar, starch, vegetable oil, or animal fats using conventional technology, and the most common are vegetable oil, biodiesel, bioalcohols, biogas and syngas. However, according to a study made by UN-Energy on sustainable bioenergy: “The substantial near- to medium-term impacts on food security will be driven largely by current-generation liquid biofuels for transportation, which depend almost exclusively on feedstock from food crops”, with this meaning security of supply and security of prices (UN-Energy, Apr 2007).

This led to the limitations of first generation biofuels:

- there is a threshold above which they cannot be produced without threatening food supplies and biodiversity;
- they are not cost competitive with existing fossil fuels such as oil;
- some of them produce only limited greenhouse gas emissions savings (when taking emissions from production and transport into account, life-cycle emissions from first-generation biofuels frequently exceed those of traditional fossil fuels).

However, on a small scale, the first generation biofuels can still be sustainable, especially if they use waste as feedstock.

Second generation biofuels can help solve these problems and can supply a larger proportion of our fuel supply sustainably, affordably, and with greater environmental benefits. Second generation biofuels use biomass to liquid technology, including cellulosic biofuels from non food crops. Many second generation biofuels are under development such as biohydrogen, biomethanol, DME, Bio-DME, Fischer-Tropsch diesel, biohydrogen diesel, mixed alcohols and wood diesel (Malhotra, 2007). The drawback of these processes is the rather immature technology.

Microalgae biofuels are considered by some as second generation biofuels, but the majority classifies them as **third generation biofuels**. They detent a major advantage face to terrestrial plants: they are much more efficient in capturing solar energy. Switchgrass for example, the fastest-growing terrestrial crop, can convert solar energy to biomass energy at a yearly rate of no more than 1 W/m^2 , less than 0.5 % of the solar energy received at a typical mid-latitude region ($200\text{-}300 \text{ W/m}^2$) (Lewis & Nocera, 2006). Microalgae, on the other hand, can have 10-20 % or more of photosynthetic efficiency. (Huntley & Redalje, 2007)

Furthermore, recent studies showed that the extra N₂O entering the atmosphere as a result of using nitrogen fertilizers to produce crops for biofuels, when calculated in “CO₂-equivalent”, could contribute as much or more to global warming by N₂O emissions than cooling by fossil fuel savings (Crutzen, 2007). The solution may be on using fast-growing microalgal species for biofuel production.

More recently, research has open up new sources of feedstock from direct production of hydrocarbons from plants or microbial systems, such as microalgae.

Amongst the different biofuels, suitable for application in transport, bioethanol and biodiesel seem to be the most feasible ones at present. The key advantage of bioethanol and biodiesel is that they can be mixed with conventional petrol and diesel respectively, which allows using the same handling and distribution infrastructure. Another important strong point of bioethanol and biodiesel is that when they are mixed at low concentrations - up to 10 % bioethanol in petrol and up to 20 % biodiesel in diesel, no engine modifications are necessary (Kavalov & Peteves, 2005).

1.1 Framework and Project Presentation

The major goal of the present study is to formulate and substantiate a map of opportunity for the present and future technologies, for its use on the conversion of different types of biomass to biofuels. The main purpose relies on the fact that to accurately plan a strategy for biofuels production it is necessary to fully understand the options available today for biofuels production.

Another goal of this report is to analyse two case-studies: to identify the most suitable and recent options for microalgae biomass conversion, and develop a biorefinery concept where the main feed corresponds to microalgae biomass.

The proposed goals may be achieved through an intensive literary search on the biomass conversion processes, which implies identifying the main biomass types and biofuels possible to obtain - inputs and outputs identification. Once identified the relevant and present conversion routes it is possible to perform an economic comparison between them through the available literature data and through a determination of total investment and operations costs for all technologies. It is also an objective to identify the trends and patterns based on evolution assessment methods such as TRIZ and Philomemetic, through literature data and also through performing a bibliometric assessment.

1.2 Work Contributions

AlgaFuel is a new company resultant from a spin-out of Necton, SA, dedicated to the development and implementation of bioengineering projects for industrial microalgae production. With more than 10

years of experience in microalgae production, AlgaFuel employs its know-how at the bidding of industry, creating opportunity for the development of technologies for carbon sequestration and production of raw material for biofuels. In the follow of this main goal, comes the interest for this project. The complete knowledge of the available options for converting microalgae into biofuels plays an important role for the implementation of projects in this area, and to efficiently add value to microalgae biomass.

1.3 Thesis Organization

The first section gives a framework on the project essential issues. In the second section is carried out a revision of the state of the art.

In the third, and most important section, are presented the main tasks developed in the project, and is given a technical evaluation and discussion of results. In the first four sections is performed an overview on the present and available biomass types, biofuels production technologies, biofuel chains and the hole integrated system. The detailed conversion processes description is available in appendix 1. Section 3.5 gives an economic assessment of investment cost for various technologies, and some estimates on biofuels final prices. The progress trends identification is available in section 3.6, based on existing studies and on a new bibliometric study on biomass conversion processes. A study on the state of technology is also performed. Finally, two case-studies are presented: section 3.7 evaluates the available technologies for microalgae biomass conversion and the identification of the relationship between microalgae biomass and correspondent conversion processes. The biorefinery concept is addressed in section 3.8, and a conversion processes flow diagram is developed for the case where microalgae are the main feed.

Finally in section 4, the most relevant conclusions are presented, and in the fifth section is given an evaluation of the performed work.

2 State of the Art

Today the major biofuel producing countries are Brazil, the USA and the EU. In Brazil and North America there is an increasing large scale production of ethanol, produced from sugar cane and corn, respectively. In Brazil at the moment, all the gasoline today has a blending of 22-26 % of ethanol, and in USA 2 % of gasoline consumption is bioethanol (Vessia, 2005). In EU the major percentage of biofuels production is biodiesel from rapeseed. However, within EU member states, there are notable differences on volume productions in the ratio between biodiesel and bioethanol. Recently biofuels consumption grew strongly, reaching an approximate 1.5 % share of EU gasoline and diesel demand in 2006 (EU Intelligent Energy - Program Refuel, 2008).

With the recent food security threat caused by 1st generation biofuels, a raising number of research projects appeared on new alternatives for fossil fuels substitution. A great number of reports, such as the present work, were made attempting to provide and integrate the existent knowledge on new alternatives for biofuels production, on a single document that allows the discussion on biofuels on a recent and comprising level. There are many examples available of reports on biofuels technologies pathways.

A study by RisØ - National Laboratory for Sustainable Energy (Larsen et al., 2003) focus on the emerging and future technological options for biofuels production, and performs an analysis on total invested money for all the renewable energy areas. Also, an extremely complete thesis report by Carlo Hamelinck (Hamelinck, 2004) focus essentially on the Fischer-Tropsch option and performs an energetic and economic assessment. Another research paper by Andre Faaij (Faaij, 2006) makes an interesting overview on present technologies and its current status. In the same year, a report “Progress and recent trends in biofuels” (Demirbas A. , 2006) makes a chemical analysis of the current technologies, and indicates pathways for every biofuel production.

EPA (United States Environmental Protection Agency) published a matrix presenting the eight major technologies being developed to convert biomass, and characterizes all technologies with regards to biomass types, biofuels produced and technical option for the process industrial implementation (Kimes & Perla, Dez 2007). An extremely complete report by George Huber (Huber et al., 2006) provides a detailed description of all the biomass types and biofuels production pathways, also in a chemical perspective.

More recently two other thorough reports appeared. The first (Briens et al., 2008) gives a thorough processes description and biorefinery overview. Another publication also (The Royal Society, Jan 2008) has an extremely good description of processes, biofuels and biorefinery concept, and provides an

overview on biofuels end use and applications, and their impacts (life-cycle assessment, GHG emissions, water, biodiversity, etc).

There has been also a large research on lignocellulosic conversion pathways, as it is a promising technology with some remaining limitations. A Norwegian report (Vessia, 2005) explores all the available options for lignocellulosic biomass, in a detailed chemical explanation. A report named “Breaking the barriers to cellulosic ethanol” (Houghton et al., 2006) performs a detailed review on the most recent advances for overcoming the limitations, also referring the GEO thematic (Genetically Engineered Organisms). A recent report by Thomas MacDonald (MacDonald, 2007) explores the alcohol fuels production, and performs an analysis on various pilot plants and commercial plants examples.

There are also two thorough studies on biofuels impact discussion (GHG emissions, food security, etc) and sustainable bioenergy: (Quirin & Gärtner, 2004) and (Karlsson, 2007). Assessments on future options and roadmaps: (EU Biofuels Technology Platform, 2008), (BMELV, 2006), (US Department of Energy, 2002), (EU Intelligent Energy - Program Refuel, 2008). Four reports with economic assessment of current commercial and pilot stage technologies are: (Thuijl et al., 2003), (GTZ, 2005), (Innovative Natural Resource Solutions LLC, 2006) and (Larson, 2008).

3 Technical Description and Discussion of Results

3.1 Biomass types: inputs identification

This section addresses the range of feedstock that can be used to produce liquid biofuels, i.e. biomass. Biomass is the plant material that derives from photosynthesis, via reaction between air and CO₂, water and sunlight. During photosynthesis, solar energy is collected in the chemical bonds of the structural components of biomass. This process converts usually less than 1 % of the available sunlight to stored, chemical energy. When the bonds between adjacent carbon, hydrogen and oxygen molecules are broken, these substances release their stored chemical energy, and if the energetic final product is combined with oxygen the carbon is oxidised to produce CO₂ and water (see figure 7). The process is cyclical as the CO₂ is then available to new photosynthesis.

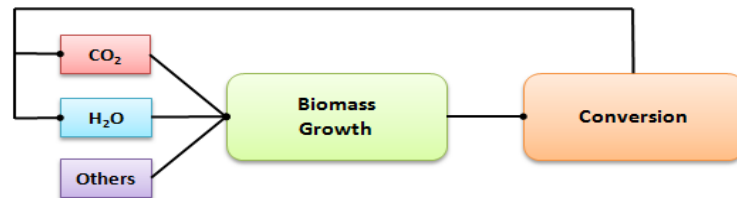


Figure 7. Biomass cycle of the CO₂ and water

This explains why biomass is considered a source of renewable energy: it is derived by means of the sun and natural processes that are replenished constantly. To ensure that this carbon neutral cycle closes, it is important the permanent cultivation and replacement of biomass. Biomass yield depends on region, soil conditions, climate, chemical requirements for output products, characteristics of the crop species/cultivar grown, environmental impacts, etc.

Researchers characterize the various types of biomass in different ways. Some characterize them according to the general biomass type designation (e.g. agricultural crops), others by the specific type (e.g. corn), others by the biomass basic units (e.g. sugar crops), but many other ways of characterization are used.

In this work the first and third ways of characterization are considered. For the characterization according to the general biomass type designation, and taking into account the alternatives given by most publications, the following organization was made (figure 8): agricultural crops and residues (e.g. excluded parts of food crops as cereal straw), forestry crops and residues (e.g. wood wastes), industrial residues (e.g. pulp and paper industrial sectors), animal residues (e.g. manure), municipal solid waste

(e.g. organic waste from food and packaging) and marine crops. As marine crops is considered macroalgae, microalgae, water weed and water hyacinth. Figure 9 presents some more examples.

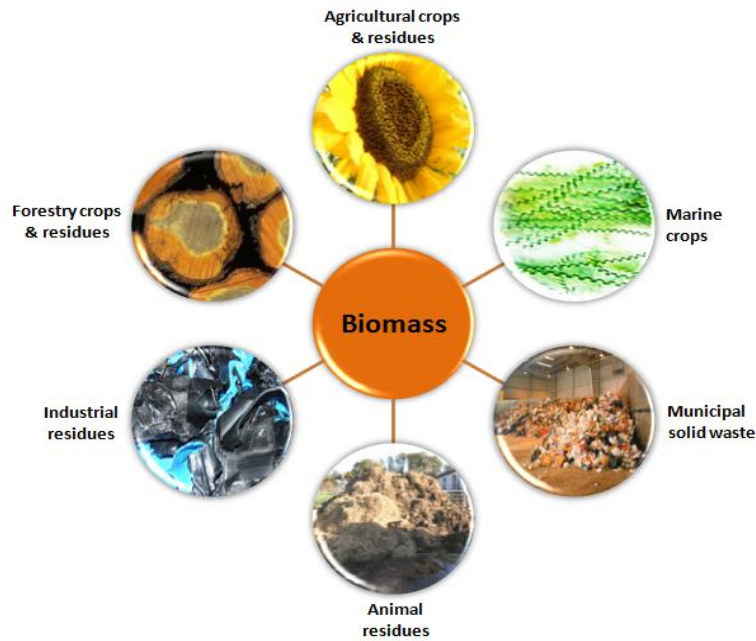


Figure 8. Biomass characterization according to its origin

Agriculture	Forestry	Industry
<ul style="list-style-type: none"> oil crops sugar starch crops lignocellulosic crops residues 	<ul style="list-style-type: none"> residues from thinning residues from harvesting 	<ul style="list-style-type: none"> sawn industry residues wood industry wastes food industry residues bark black liquor sewage sludge

Figure 9. Examples of the type of materials included in each category

An important type of characterization is that where biomass basic units are the element of distinction. In this way, is possible to distinguish the biomass by the elements that will influence the type of conversion pathway, to obtain a certain biofuel. Note that a second type of distinction is made: the moisture content. Any high moisture materials can be included in the “wet biomass” categorization, and this subsequently dictates a different form of conversion process.

Within the categorization of figure 10, all the residues from sugar crops, starch crops and oil crops are essentially constituted by cellulose, hemicellulose or lignin, and for that reason they are included in

the lignocellulosic biomass. Some examples of where it is possible to find every category of biomass basic units are represented in figure 11.

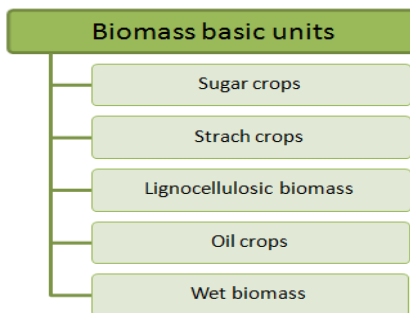


Figure 10. Biomass characterization according to its basic units

Sugar crops	Starch crops	Lignocellulosic biomass	Oil crops
<ul style="list-style-type: none"> • sugar cane • sweet sorghums • sugar beet 	<ul style="list-style-type: none"> • maize • sorghums • wheat 	<ul style="list-style-type: none"> • sugar crop residues • starch crop residues • oil crop residues • woody crops • grasses • hydrocarbon plants 	<ul style="list-style-type: none"> • castor bean • corn • rapeseed • sunflower • canola • coconut • olive • palm • microalgae

Figure 11. Examples of biomass basic units origin

Sugar is a class of edible crystalline substances including sucrose, lactose, and fructose. Sucrose is a disaccharide of glucose and fructose, with the molecular formula $C_{12}H_{22}O_{11}$. Lactose has the chemical formula $C_{12}H_{22}O_{11}$ and fructose is a simple reducing sugar (monosaccharide) with the chemical formula $C_6H_{12}O_6$ (Huber et al., 2006).

Starches are glucose polysaccharides with chemical formula $(C_6H_{10}O_5)_n$, that have α -1,4 glycoside linkages, but also have a large amount of α -1,6 glycoside linkages. These α linkages make the polymer amorphous. All plant seeds and tubers contain starch which is predominantly present as 20-25 % amylose and 75-80 % amylopectin (Huber et al., 2006).

The structural materials that constitute plants in its cell walls, stems, stalks and woody portions of biomass are composed mainly of three biobased chemicals: cellulose, hemicellulose and lignin, which are globally called as lignocellulose (figure 12). Typically, dry lignocellulose biomass contains 40-50 wt % cellulose, 25 wt % hemicellulose and 25 wt % lignin (The Royal Society, Jan 2008).

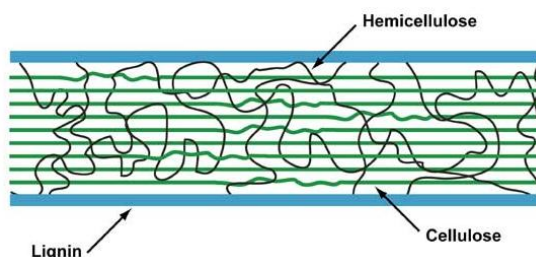


Figure 12. Structure of lignocellulose (cellulose, hemicellulose and lignin)

Cellulose is a very large polymer molecule composed of thousands of D-glucopyranose monomers, also called polysaccharide. The β -1,4 linkages between D-glucopyranose molecules form linear chains that are rigid, highly stable, and resistant to chemical attack. Unlike starch, cellulose is a crystalline substance with an extended, flat, 2-fold helical conformation. The degree of polymerization of cellulose is approximately 10 000 to 15 000 glucopyranose monomers in wood and cotton, respectively. (Rutz & Janssen, 2007)

Hemicellulose, in contrast to cellulose which is a polymer of only glucose, is a mixture of polysaccharides of five different sugars. It contains 5-carbon sugars as xylose and arabinose, and 6-carbon sugars as galactose, glucose and mannose. In contrast to cellulose, it is a heterogeneous branched polysaccharide that binds tightly, but not covalently, to the surface of each cellulose microfibril. (Rutz & Janssen, 2007)

Different types of **lignin** have been described. Lignin is a large macromolecule, whose building blocks are believed to be a three carbon chain attached to rings of six carbon atoms, called phenyl-propanes. These may have zero, one or two methoxyl groups attached to the rings. (Rutz & Janssen, 2007)

Oils, fats or triglycerides consist of water insoluble, hydrophobic substances that are made up of one mol of glycerol and three mol of fatty acid. Oil crops are also viscous liquids at ordinary temperature, less dense than water. (The Royal Society, Jan 2008)

3.2 Biomass conversion system

Economic and technical viability of this system depends on a guaranteed feedstock supply, effective and efficient conversion technologies, guaranteed markets for the energy products, and cost-effective distribution systems. There are four important fields on the biomass conversion system that are currently being deeply researched, represented in figure 13.

The first, biomass resources, was described in section 3.1. Once it has been proven that some energy crops, like corn, are threatening the supply and prices, they have been left aside and new energy crops are being considered, like lignocellulose and microalgae. This issue includes, beside the choice of the most suitable energy crops, the production system, maintenance and collect of the biomass.

Feedstock processing includes all the treatment that the biomass has to pass through, before the conversion step. Sometimes the conversion process may become more economically viable, when the biomass passes through an efficient step of pre-treatment.

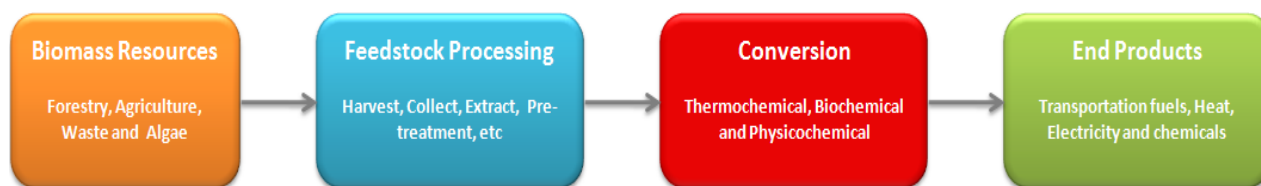


Figure 13. The biomass conversion system

The most important step in this system is the biomass conversion step. Depending on the feedstock and on the fuel, conversion may be performed through several different routes as biological, thermal and physical conversion processes. In general, biological processes are relatively slow but can deliver a well defined product, which is readily purified, although it may have substantial energy or capital costs, while thermal processes are rapid but generally deliver a mixed product that is more difficult to purify and refine to a useful product. The overall energetic efficiency of the conversion process is also affected by the amount of pre-treatment, as it was mentioned before, or transportation that is required before conversion.

Finally, after this three first steps, the end products are obtained. Many research projects are focused on the production of heat and electricity from biomass. However, in this work, only the production of biofuels is being studied.

3.3 Evaluation of the Biomass Conversion Processes

This section describes and explains the *Biomass Conversion Map* (figure 16). This map is the centrepiece of this work, as it exposes all the present significant technologies available to perform the conversion of biomass into biofuels. It displays the biomass system from feedstock through intermediate products, and conversion to the final products.

The complexity of the system is based on the fact that, a variety of products may be created from a given feedstock and a particular final product may be derived from different feedstocks and conversion technologies.

3.3.1 Identification of Inputs and Outputs of the Technology

This section tries to illustrate the technology options available, for biofuels production from biomass (biofuels pathways).

As explained on the section 3.1, the type of categorization of the system input (biomass resources) is very important since it influences the entire *Biomass Conversion Map* pathway. The categorization assumed in this work refers to figure 10, where the biomass resources are distinguished by their basic chemical structure. This type of categorization facilitates the choice of the conversion pathway, as the conversion processes are very dependent of the chemical structure of the biomass.

Before analysing the outputs of this complex system, it becomes necessary to identify the general routes of biomass conversion. There are three types of technology routes to convert biomass into useful biofuels: biochemical, thermochemical and physicochemical.

Biochemical Conversion

This route uses microorganisms to perform the conversion of biomass feedstocks to energy, typically in the form of liquid and gaseous fuels. Microorganisms are regarded as biochemical “factories” for treating and converting most forms of organic waste. This pathway can ensure also the production of electricity, heat and bioproducts.

Thermochemical Conversion

This pathway does not necessarily produce useful energy, instead it uses controlled conditions of temperature and oxygen level to convert the feedstock into more convenient energy carriers such as synthesis gas and bio-oil that can be later converted into biofuels. This technology has also the potential to produce electricity, heat and bioproducts.

Physicochemical Conversion

Physicochemical technologies use chemical agents or physical processes to convert biomass feedstocks to energy, typically in the form of liquid fuels.

In figure 14 are represented the most important processes of each conversion pathway.

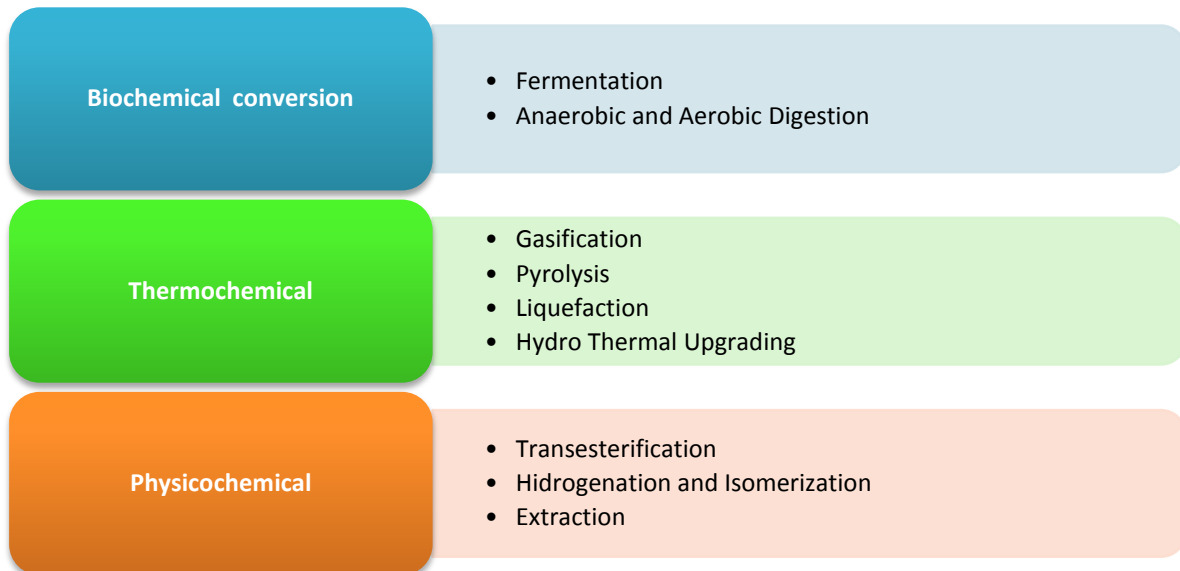


Figure 14. Most important processes within the technology routes for biomass conversion

All the indicated processes, within each technology route, have pre-treatment or subsequent conversion steps, fact that originates the complexity of the *Biomass Conversion Map*. This leads to a great number of outputs (biofuels), because within the same conversion process it is possible to have different biofuels depending on the subsequent conversion step.

Although only biofuels are represented as outputs, the same biomass feedstocks can also be used for electricity (biopower) generation, as well as for chemicals production, production of food products, animal feed and various other beneficial products or by-products.

Figure 15 is a simplified representation of the conversion pathways, with the correspondent inputs and outputs.

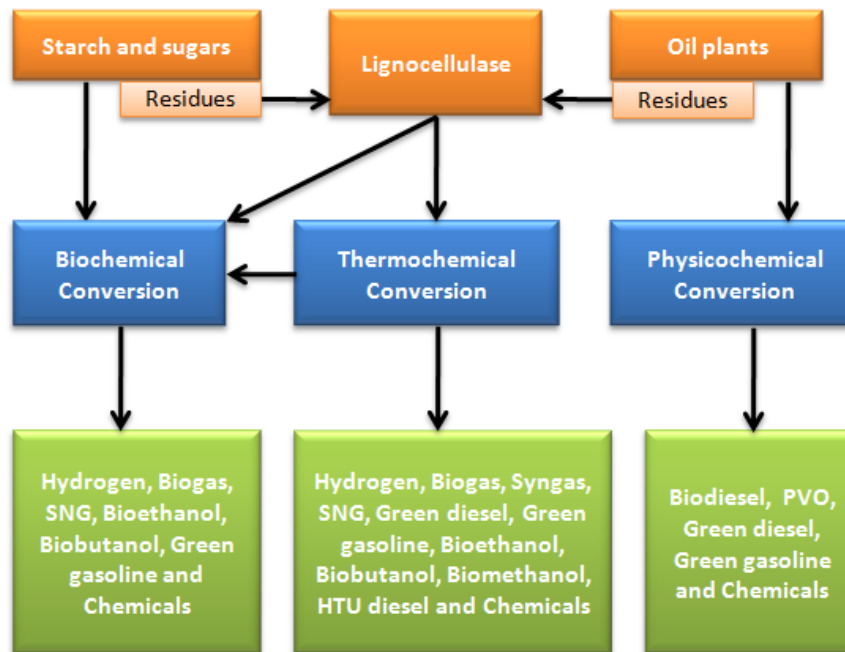


Figure 15. Inputs and Outputs of the biomass conversion routes

3.3.2 The *Biomass Conversion Map*

Figure 16 shows the centrepiece of this work, the *Biomass Conversion Map*, which involves the study of almost all available publications on biofuels production processes. Only the most important and general processes are referred, although some of them may vary quite a lot depending on the type of technology involved to perform it.

A detailed description of the processes included in the Biomass Conversion Map will be presented in appendix 1.

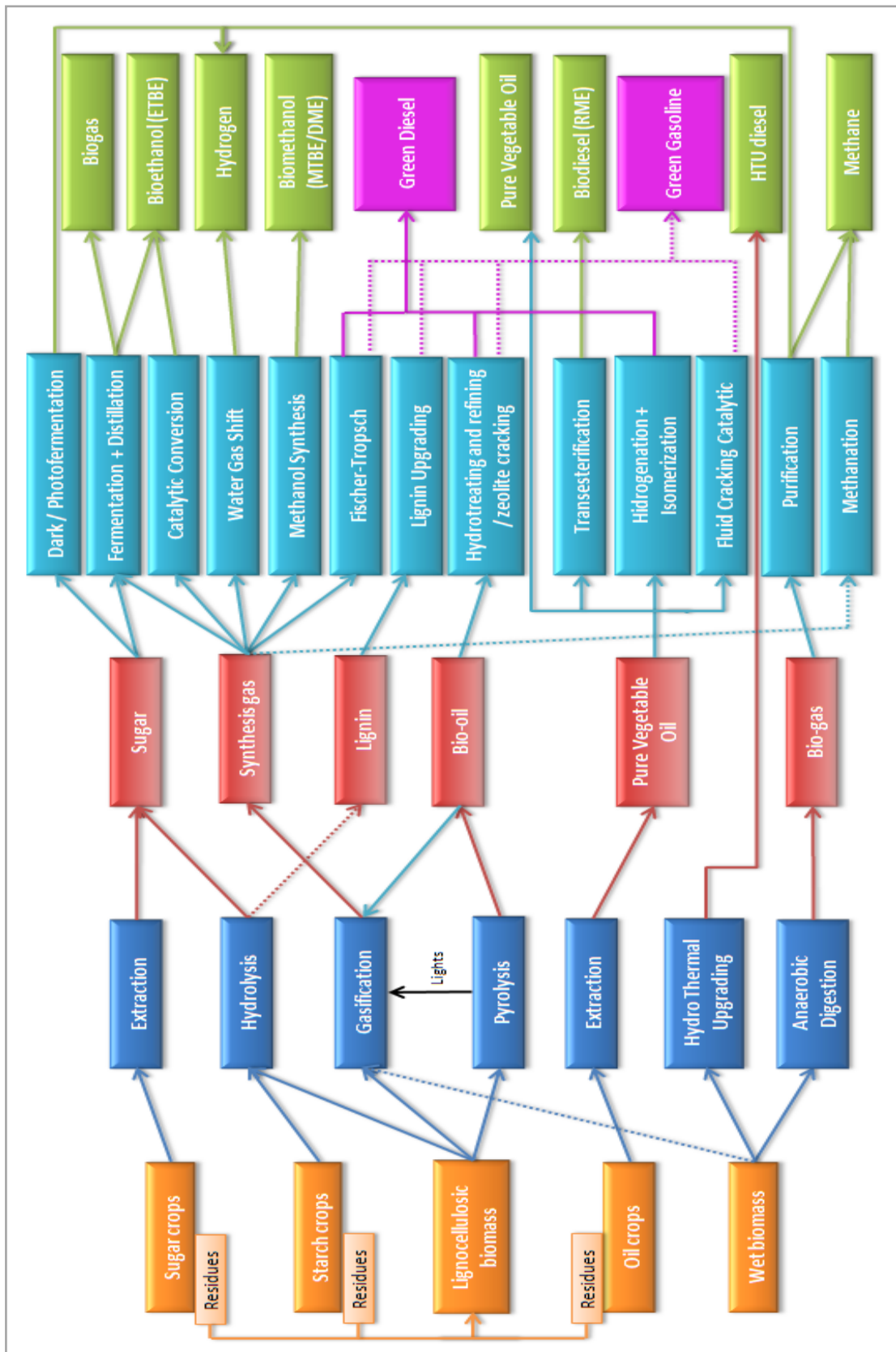


Figure 16. Biomass Conversion Map

3.4 Biofuels Overview

As mentioned before, for fuels produced from biomass, various conversion routes are possible. For each route, the fuel characteristics of the biofuel are different. In this section, these characteristics will be described, as well as some information about its usage on current fossil fuels engines [(Rutz & Janssen, 2007), (Nylund et al., 2008), (Kampman et al., 2005) and (Thujil et al., 2003)].

The described biofuels that are already commercially available are PVO, biodiesel, bioethanol, biomethanol and gaseous fuels as SNG and biogas.

Pure vegetable oil

Pure vegetable oil is produced by extraction of oil crops like rapeseed, soybean and jatropha, among others. Its composition is based on triglycerides, chains of fatty acids. It is not appropriate for use as single fuel on conventional engines, because of its high viscosity and higher freezing point.

Biodiesel

Biodiesel is the designation of all ethyl or methyl esters derived from vegetable oils. Esterified vegetable oils are suitable for application in automotive diesel engines as its viscosity, density and cetane number are similar to those of diesel. However its slightly higher viscosity affects the atomisation of the fuel during the injection, and it has problems in the cold start behaviour of the engine, what can be solved by fuel heating. Also its higher oxygen content leads to higher fuel consumptions. As blend for fossil diesel it can be used in any proportion, but for 100% biodiesel usage, a number of relatively minor changes in the engines are required.

Bioethanol

Bioethanol is an alcohol that can be produced from sugar or starch, derived from sugar crops, starch crops or lignocellulosic biomass. Ethanol is best used in a spark ignition or Otto engine because of its high octane rating. Due to its poor ignition quality (low cetane number), ethanol is less suitable for diesel engines. As advantages, the octane number appears to be higher than that of gasoline, and lower oxygen content (lower oxygen content makes the fuel have higher calorific value). However, the low vapour pressure of ethanol, together with its single boiling point, is disadvantageous with regard to engine start at low ambient temperatures.

ETBE

Bioethanol can be converted to ETBE, which can be used to replace MTBE, a constituent of gasoline. While only 1-5% of MTBE can be incorporated to gasoline, with ETBE the blend may be of 15% or higher.

Biobutanol

Like bioethanol, biobutanol is an alcohol, however it emits low vapour pressure, has tolerance to co-existence with water contamination in gasoline mixtures and may be used as blend in higher concentrations than bioethanol (sometimes 85 % with minor or no vehicle modifications). This biofuel also produces superior fuel economy compared to gasoline-bioethanol blends. (Ezeji, 2007)

Bio-oil

Bio-oil, also called pyrolysis oil, bio-crude or biofuel-oil is a black liquid similar to fossil oil produced through pyrolysis. With this process, a liquid is produced as intermediate for a wide variety of applications, for example as feed for chemicals production. It cannot be used in conventional gasoline and diesel engines because of corrosion and plugging. For use as a transportation fuel it needs to be upgraded and stabilised to diesel quality first, producing a liquid called green diesel. The main differences between bio-oil and fossil oil are its higher density, lower energy content due to its high content of organically bound oxygen, less content of nitrogen and almost no metal and sulphur components. Also, it does not mix with hydrocarbons but is soluble in water.

HTU-oil and HTU-diesel

The product of HTU conversion is HTU-oil, much similar to fossil oil than bio-oil. It is a viscous black organic liquid, a mixture of various kinds of hydrocarbons. As it has low oxygen content (high calorific value), it is not mixable with water as bio-oil, and is also more stable. As advantage, it also has a very low concentration of nitrogen and sulphur. It can be separated into light and heavy HTU-oil. The heavier fractions which contain all minerals can be used for naphtha or chemicals production. The lighter fractions, which are very clean, can be used for the production of HTU-diesel by catalytic deoxygenation.

For the referred reasons, HTU-diesel is expected to have very good qualities as the cetane number is higher than conventional diesel (better ignitability), the fuel is clean and does not contain oxygen. This means it can be mixed with conventional diesel in any proportion, or it can be applied in the existing diesel engines and distribution infrastructures.

Biomethanol

Biomethanol, as bioethanol, has been used for transportation for quite a long time. It can be produced from synthesis gas. As it has a low cetane number, it has poor ignition quality, what makes it unsuitable for diesel substitution. Since it has a high octane rating it is preferred as gasoline substitute, and for less than 15 % of incorporation it may be used in regular gasoline engines without modification. For its application in higher proportion or in pure form, the necessary adjustments of the engine are the same as for ethanol due to its similar characteristics.

DME

It can be produced from methanol through a process of catalytic Dehydration, or from synthesis gas of biomass gasification. It can be used as a substitute for liquefied petroleum gas, diesel and gasoline. However, it is a gaseous ether and water soluble.

Synthesis gas

This gas is the resulting product of gasification, and is mainly composed of carbon monoxide and hydrogen. It is the feed of the technology Biomass-to-liquid, which includes various processes that convert this gas into valuable biofuels.

Green Diesel and Green Gasoline

In this report this categorization includes all the biofuels with very similar properties as conventional diesel and gasoline, which can be used without engine modifications.

Biogas and Methane

Biogas is produced from anaerobic digestion of organic materials or fermentation of sugars, and has to be purified before it can be used as fuel. Its components are CH_4 , CO_2 and nitrogen. It can further be used to produce hydrogen. Methane can be used in the same way as natural gas.

A study on GHG emissions and energy cost balance for some biofuels is presented in appendix 2, where it is possible to verify that the biofuels that allow higher savings on GHG emissions are bioethanol from sugar beets and wheat, and biodiesel from rapeseed. In terms of primary energy savings, the best results are for bioethanol from sugar beets, wheat and potatoes, and for hydrogen. The referred energy savings of the fossil fuels replacement by biofuels are related to the differences in their energy content. Figure 17 gives some biofuels energy density.

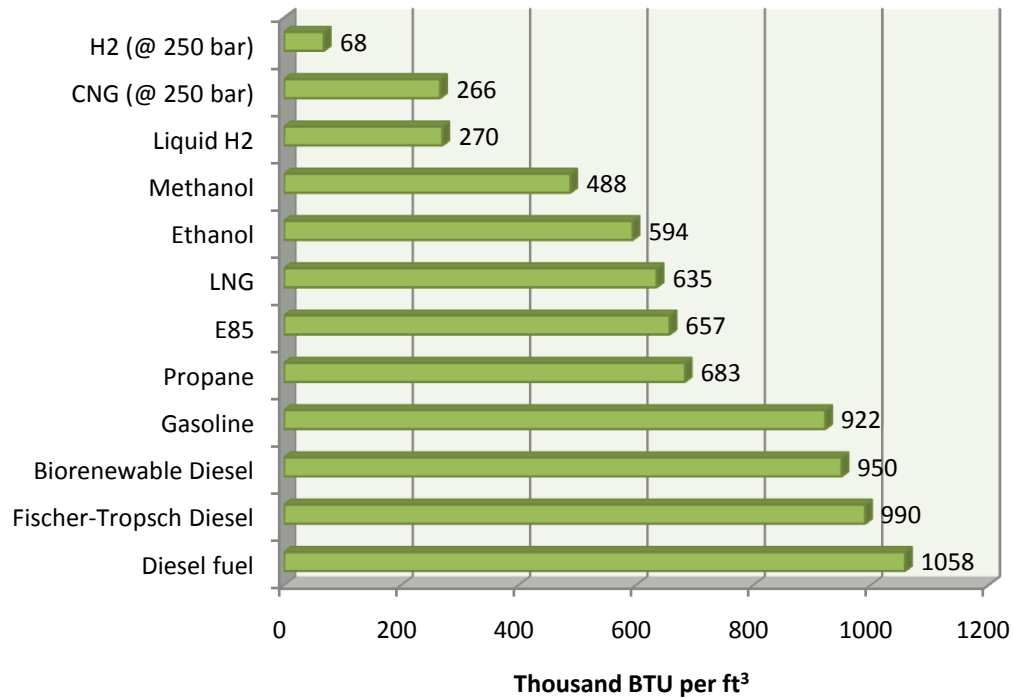


Figure 17. Energy density of various biofuels - adapted from (Nylund et al., 2008)

As it can be observed in figure 17, bioethanol energy content is lower than gasoline, which means that for the same drove distance is spent more bioethanol than gasoline. When bioethanol is used to blend gasoline, 5.0 % ethanol on an energy basis should be 7.5 % on volume basis.

A study made by Nils Nylund presents the necessary engine adaptations to perform, for the utilization of each biofuels as replacement for fossil fuels (Nylund et al., 2008).

3.5 Economic Assessment

3.5.1 Technology associated costs

All the technologies presented in appendix 1 have different process costs. For the technologies that are already proven in a commercial scale (as transesterification and starch & sugar fermentation) this cost values are available, but some technologies still run on pilot facilities, and some others are not more than lab tests. For these processes only pilot data and scale-up information are available, so the cost values found on literature represent only estimates. A realistic economic assessment of biomass conversion processes would involve a long and extremely thorough analysis, because feedstock and process equipments prices continuously change, processes are continuously developed, scale-up

information and estimates are sometimes unrealistic, among other reasons. In table 2 are presented some estimate values, from various research projects. The highest investment corresponds to BTL technologies: FT diesel, DME and methanol production.

Table 2. Processes total Investment estimates from several researches [values actualized through the CEPCI Index - Chemical Engineering Plant Cost Index - to a 2007 basis (Chemical Engineering magazine, www.che.com)]

Biofuel	Process	Total Investment (million €)	Unit capacity	Source
Green diesel	Hydrogenation + Isomerisation	13-21	300 000 MT / year	(Kalnes, Marker, & Shonnard, 2007)
Bioethanol	Simultaneous Saccharification & Co-Fermentation	130,4	2 000 MT / day	(Aden, 2007)
HTU diesel	HTU	230,0	330 Kton / year	(Goudriaan, Naber & Berg, 2006)
HTU diesel	HTU	49,7	400 MW	(Thuijl, Roos & Beurskens, 2003)
HTU diesel	HTU + Hydrodeoxygenation	279,7	400 MW	(Thuijl, Roos & Beurskens, 2003)
Methanol	Gasification + Methanol synthesis	366,0	400 MW	(Thuijl, Roos & Beurskens, 2003)
DME	Gasification + Methanol synthesis + Catalytic Dehydration	509,7	200 000 ton / year	(Thuijl, Roos & Beurskens, 2003)
FT diesel	Gasification + FT synthesis	376,4	400 MW	(Thuijl, Roos & Beurskens, 2003)
HTU diesel	HTU	20,1	7 ton / h	(Koppejan, 2004)

However, there are some interesting studies, where the available data may provide some conclusions. This is the case of the data presented in figure 18, where the information was adapted from a study named *Refuel*, provided by *ECN Policy Studies*.

This study shows that O&M cost variations within these technologies, are not so discrepant as for investment costs. For the investment costs, the highest values correspond to lignocellulosic biomass fermentation, and to conversion of synthesis gas into CH₄ (SNG) and methanol. The lowest values are from conversion of synthesis gas to Fischer-Tropsch synthetic diesel and gasoline, sugar fermentation and PVO from oil extraction, besides of course the biogas production that is for definition a low cost technology.

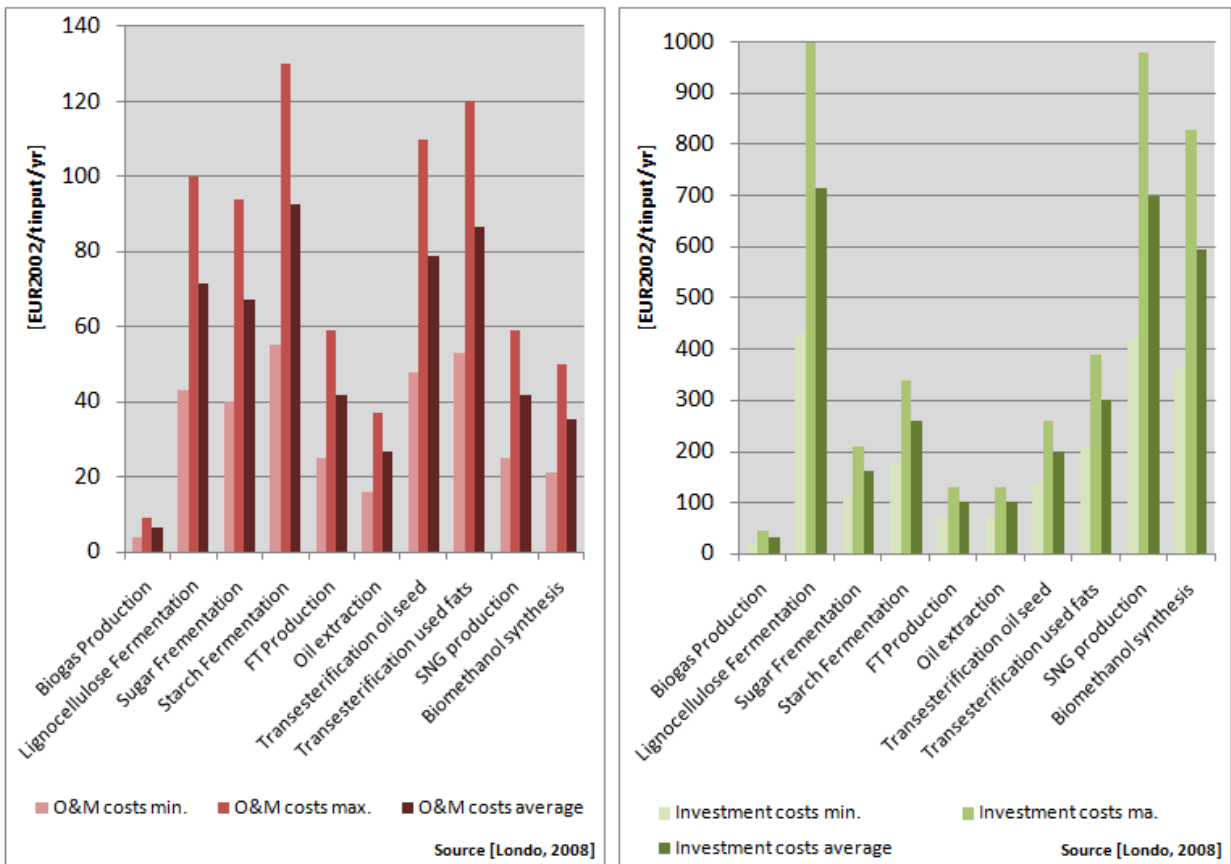


Figure 18. Some biofuels O&M (left) and Investment (right) production costs, adapted from (Londo et al., 2008)

Another interesting study, shown in figure 19, and performed by the *University of Massachusetts* gives a comparison between fast pyrolysis and HTU. Both technologies produce a bio-crude type liquid that can be either upgraded into synthetic fuels, or used directly as feed for a conventional fossil oil refinery.

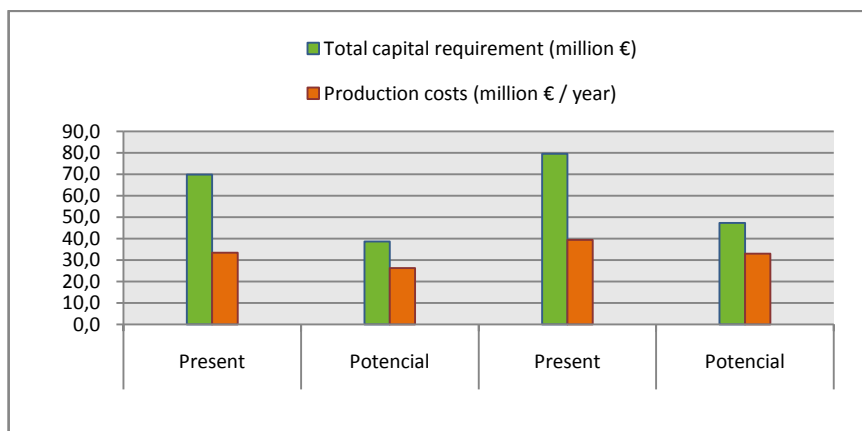


Figure 19. Fast pyrolysis and HTU process costs comparison - adapted from (Huber, 2008)

It can be observed that both production costs and the total capital investment, are higher for HTU conversion process. Note that the value presented in this chart is in the millions order, contrary to the previous chart. This is explained by the fact that, in the previous study the values were correspondent to cost per year and per tonne of biofuel produced, and in this study are only represented per year. This research also indicates that if these bio-crudes were integrated in a conventional fossil oil refinery, the production cost of the biofuels based on current technologies, including feedstock costs and processing costs, are estimated to be in the range of US\$ 60-120 /barrel of oil equivalent, lower than the barrel price currently, in the order of US\$ 130 (on July 21th).

In appendix 3.1 it is possible to analyse two other studies on technologies economic comparison (figure 39 and 40). The first study compares the production of green diesel by two processes: gasification & FT synthesis and fast pyrolysis. The result is that gasification & FT synthesis has an extremely higher total capital cost (341 million US\$), over fast pyrolysis (28.4 million US\$). From second study the conclusion is essentially the same: FT synthesis is the process with higher investment cost, followed by methanol synthesis, but bioethanol from sugar crops is the biofuels that presents higher production costs.

The study of figure 41, also in appendix 3.1, attempted to express the relation between the feed costs and processing costs to produce transportation fuels from bio and fossil feedstock, i.e. from lignocellulose, starch and vegetable oil, as well as from crude oil and natural gas.

Analyzing the graph is possible to observe that the cost of oil refining is dominated by feed cost whereas the costs of lignocellulose conversion (through gasification and subsequent Methanol or Fischer-Tropsch synthesis) are dominated by technology. On the other hand, biofuels obtained from vegetable oil have the same economic behavior as fossil fuels, being dictated by feed costs.

3.5.2 Biofuels final prices

The 1st generation bioethanol, biodiesel, PVO and biomethanol are currently the only commercially available. World ethanol market prices varied between 0.20 and 0.30 €/L between 2001 and 2004. These figures are considerably higher in Europe where total bioethanol costs (wheat origin) vary from 0.60 up to 1.18 €/L with an average figure of 0.74 €/L. In the case of bioethanol from sugar beet, the average figure for EU-15 is slightly lower with 0.60 €/L. Biodiesel production costs in the EU-15 vary from 0.58 up to 0.9 €/L with an average figure of 0.75 €/L.

For the biofuels that have been produced only on a pilot scale, many estimates were made. Three recent studies comparing biofuels prices are presented in appendix 3.2. The main conclusions on the three studies are that ethanol from lignocellulose, biodiesel from vegetable oil converted by transesterification, and FT liquids are the most expensive.

A table with various estimates for biofuels prices, by many other researchers, is available in appendix 3.2. Within this table is an estimate for microalgae fuel price from microalgae that directly produce hydrocarbons, so there is no conversion method, only harvesting is necessary. As can be observed in that table, bioethanol from lignocellulosic and FT diesel are the biofuels with highest price values. However, it is also possible to verify that there is a great discrepancy between the estimates given by the presented researches.

3.6 Technology Progress Trends

Many researchers predict that automotive technology is moving towards electric power trains and this could mean either advanced battery electric vehicles, alternatively plug-in hybrids or hydrogen fuel cell vehicles. In the meantime combustion engines will continue to be used. What is certain is that synthetic fuels show better performance than traditional fuels, and are expected to gain importance in the long run.

In relation to synthetic fuels, current investment and technology choice is largely driven by policy targets and by high oil prices. This is leading to different regions promoting different technologies, based on the economics as well as the available feedstocks. A good example of that is the biggest consumption of bioethanol in Brazil and EUA, face to EU. In EU the most consumed and researched is biodiesel (The Royal Society, Jan 2008).

All the issues related to biofuels and presented before, as environmental impact, production costs, final fuel price, energy content, engine performance among others, may influence the development trends of biofuels technologies, but the economic and energetic balance will certainly be the most influent.

In the future, after biofuels, some researchers envisage a day when one single energy solution will cover the needs of all energy sectors. That solution may be nuclear energy based on fusion instead of today's fission reaction (Nylund et al., 2008).

3.6.1 State of Technology and main progress trends

A presentation by Jungmeier on the *Biomass & Bioenergy Conference 2008* (Estonia) included an interesting study on the state of biofuel technologies (figure 20).

It can be seen that most technologies have already passed from lab-scale to pilot plants, and many others have already been scaled-up. Biomass-to-Liquid technologies are the most advanced in the pilot plant phase, followed by lignocellulosic bioethanol. A study by George Huber (appendix 4, figure 45) also indicates the state of some technologies, but explains the challenges that every technology is facing to develop.

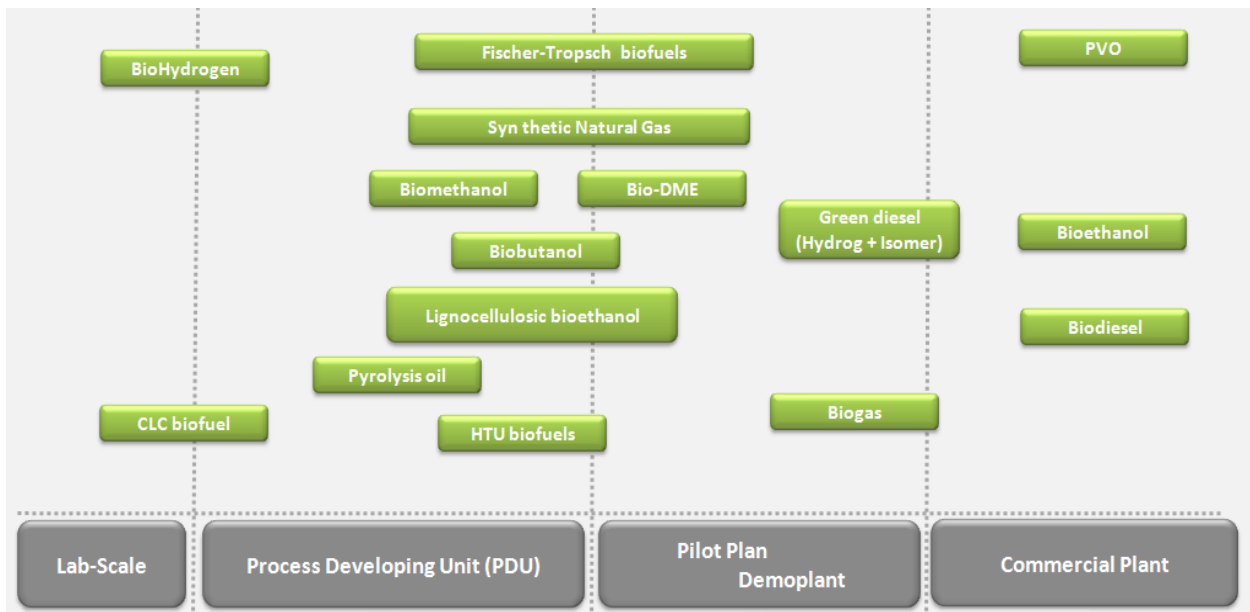


Figure 20. Map representing the state of biofuels production technology [Adapted from: (Jungmeier, 2008)]

Another study by NREL, available in appendix 4 (figure 46), presents a map indicating the maturity of many technologies as well as their major benefits. They present diesel / jet fuel from microalgae and hydrocarbons from biomass as the ultimate technologies. The referred hydrocarbon from biomass concept is related to the conversion of biomass derived components such as carbohydrates, lignin and triglycerides. According to NREL, this fuel can be used in heavy-duty vehicles, jet engines and others applications that need fuels with higher energy contents than those of ethanol or biodiesel (Ashworth, 2006). A publication by University of Massachusetts Amherst indicates that a process that allows this type of conversion is aqueous-phase processing, a multi-step process (Huber, 2008).

An island map concept (patent of Aureka) was performed for analysing the evolution on biofuels technologies, and is presented on figure 21 and 22 (Hastbacka, 2005). The first figure presents the innovation areas related to biofuels production.

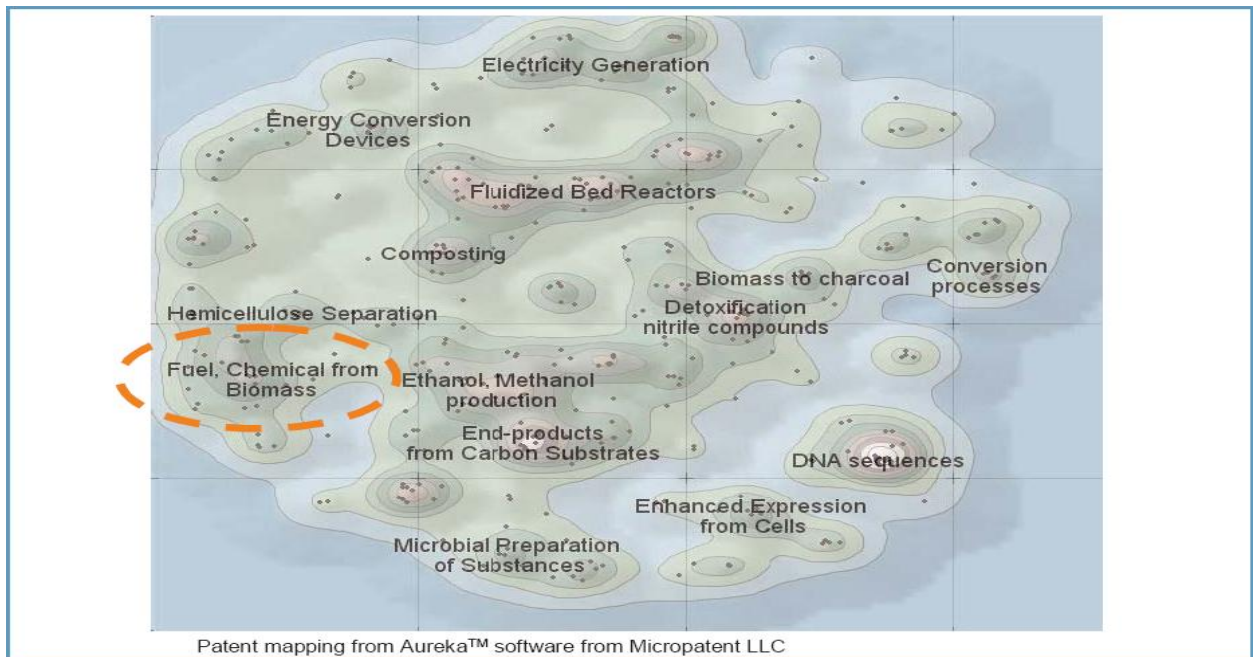


Figure 21. Areas of Innovation: Technologies Related to Biomass Conversion (Hastbacka, 2005)



Figure 22. Technologies Related to Fuels and Chemicals from Biomass Conversion (Hastbacka, 2005). Note: USPTO - United States Patent and Trademark Office, EP/PCT - European Patent Office / Patent Cooperation Treaty / JAPIO - Japan Patent Information Organization

Biomass trends

As described in section 3.1, biomass is constituted of primary products like agricultural crops, wood or aquatic biomass as well as secondary products like crop residues and organic waste e.g. from households and agricultural industries. The biomass resources that currently represent the higher potential are lignocellulosic biomass, microalgae, jatropha curcas and kudzu. The major limitation on lignocellulosic biomass is that it is a limited resource since the land where it can be grown is limited and because crop and forest residues are to a certain extent needed for preserving the fertility of the soil which is important to remember when addressing biomass resources for energy.

Biomass like organic waste from industry and households, is a biomass resource which is expected to increase in importance as a source for bioenergy, with a stronger emphasis towards recirculation (Østergård, 2007).

Alcohol trends

A lot of effort is invested in the development of processes for lignocellulosic ethanol. However, the process technology still needs development like new enzymes production. In addition, agricultural fibers have low density, thus shipping and storing as well as harvesting are costly.

Another development path is research on heavier alcohols. In 2006, BP and DuPont joined forces to develop 2nd generation bio-components for gasoline, and the first product will be biobutanol. They announce that biobutanol is expected on the market in 2007, and that existing ethanol capacity can be retrofitted to biobutanol production, which can utilize a variety of feedstocks like sugar cane, sugar beet, corn, wheat, cassava and sorghum, but in the future feedstocks such as lignocellulosic biomass could be used.

Microalgae biodiesel

The production of biodiesel obtained from easily accessible waste streams, such as vegetable oil from restaurants, is not viable because the volume of these streams is not sufficient for large-scale production. An alternative source of biodiesel is that derived from microalgae. Microalgae operate closer to the theoretical maximum efficiency of photosynthesis, and large-scale experiments suggest a several-fold increase in biomass production per area over even the best terrestrial energy crops. Furthermore, this biomass can be produced with a very high lipid content, 30-80 %, depending on the species, making the refinement process easier. In section 3.7 this issue will be exposed on detail.

Biofuels as the new oil in conventional refineries

Since 2006, the driving forces working in favor of biofuel diffusion, appear stronger than those working against by the European upstream oil industry. So is possible that recent political changes at the EU

have removed the major obstacles to the diffusion of biofuels in Europe. According to Eikeland, this should increase the future prospects for bio-energy in Europe and the pressure on oil companies to choose biofuels as the new oil to help the diversification strategy for the renewable energy products so highly announced in the past decade (Eikeland, 2006).

Nanotechnology

Nanotechnology role in biofuels production is quickly rising, and in very different fields. The major developments are in the catalyst area, where nanotechnology has an important influence. This area is extremely important in biofuels production, as almost all the processes referred in the present work have catalysts involved. A report of *Nanowork Spotlight* refers that they are important because nanosieves can save energy in biofuel production, in clean energy production and to reduce GHG. Another article on *Nanotechnology Development Blog* also refers that genetic engineering is an emerging area that is in the domain of nanotechnology, working at the molecular level in order to create "engines of creation". This may be determinant for developing better feedstocks, break down plant material into their building blocks (sugars), and then finally convert them into ethanol. They also refer that nanotechnology can be used to create other fuels such as biobutanol and hydrocarbon fuels.

Genetically Engineered Organisms (GEO)

GEO or GMO (genetically modified organisms) are organisms altered using recombinant DNA technology. This is probably the research with the most promising scenario. It is developing in different areas, one of them the production of genetically modified enzymes that ferment both C5 and C6 sugars. In this way, researchers are trying to turn the lignocellulose conversion economically viable. According to a paper by James S. McLaren, another research is focusing on GEO for increase the biomass systems for solar energy capture. He also refers that further development of biotechnology and genomics tools will enable the development of crops with specific traits that are optimized for biofuels (McLaren, 2005). An article by Richard Lugar on *Foreign Affairs*, named "The New Petroleum" refers that genetically engineered biocatalysts and new processing techniques may allow the usage of most plant matter as fuel. Another thorough article named "Microdiesel: *Escherichia coli* engineered for fuel production" by Rainer Kalscheuer, mentions an engineered bacteria for what they call microdiesel production. The "microdiesel" process avoids the use of methanol, because instead scientists engineered a specific form of *Escherichia coli* bacterium. The result is that once the modified *E. coli* is allowed to work on the vegetable oil, it produces its own ethanol which acts as a substitute for the toxic methanol (Kalscheuer & Stölting, 2006). Craig Venter, an American biologist, announced recently that he and his research team is developing a new engineered organism that will be able to produce biofuels directly from CO₂, in large bacteria-processing fermenters (Jacquot, 2008).

Microalgae producing hydrocarbons approach will be further developed in section 3.7

A study named “Vision Report” by EC (appendix 4, figure 47), summaries the future of biofuels technologies development (Rutz & Janssen, 2007). The global idea is that in a recent future 2nd generation biofuels will replace the present ones, and by 2030 integrated biorefineries will prevail, with production of biofuels and high value co-products. Another study by Ecofys Academy (appendix 4, figure 48), establishes that from 2020 forward, biodiesel and bioethanol may fading out and lignocellulosic biofuels take place (Harmsen, 2008).

3.6.2 Bibliometric Patterns

A way of estimating the potentials and trends for new and emerging technologies is by looking at indicators for innovation based on bibliometric searches. Figure 23 represents the annual number of biomass conversion technology papers.

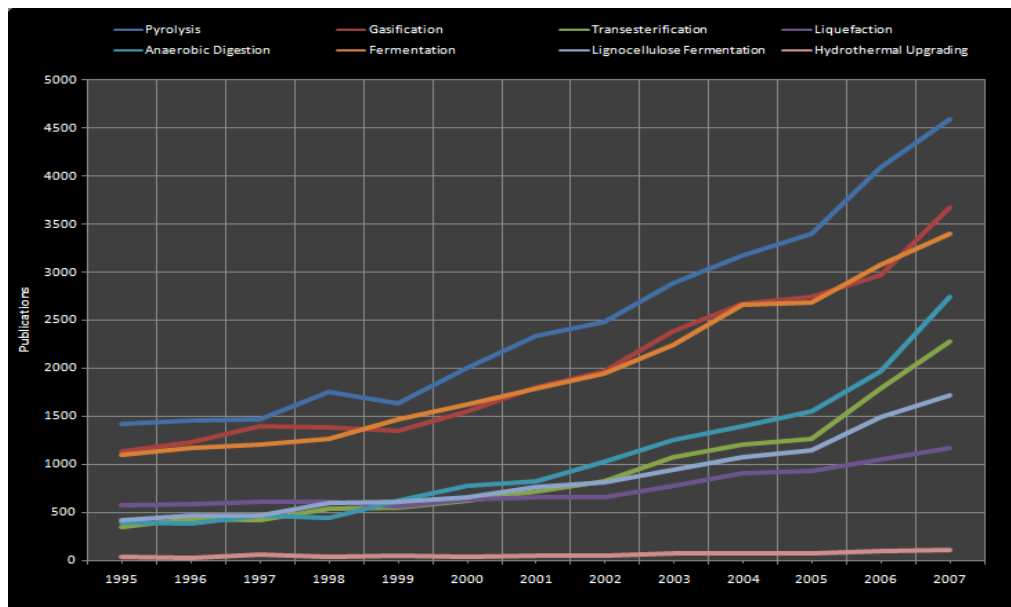


Figure 23. Annual number of publications on each technology research since 1995 (data obtained using Google Scholar)

It can be seen that all conversion process technologies have been exhaustingly researched in the last years, rising incredibly since 1995. However, this type of conclusion brings no advantages trying to understand a tendency on technology evolution.

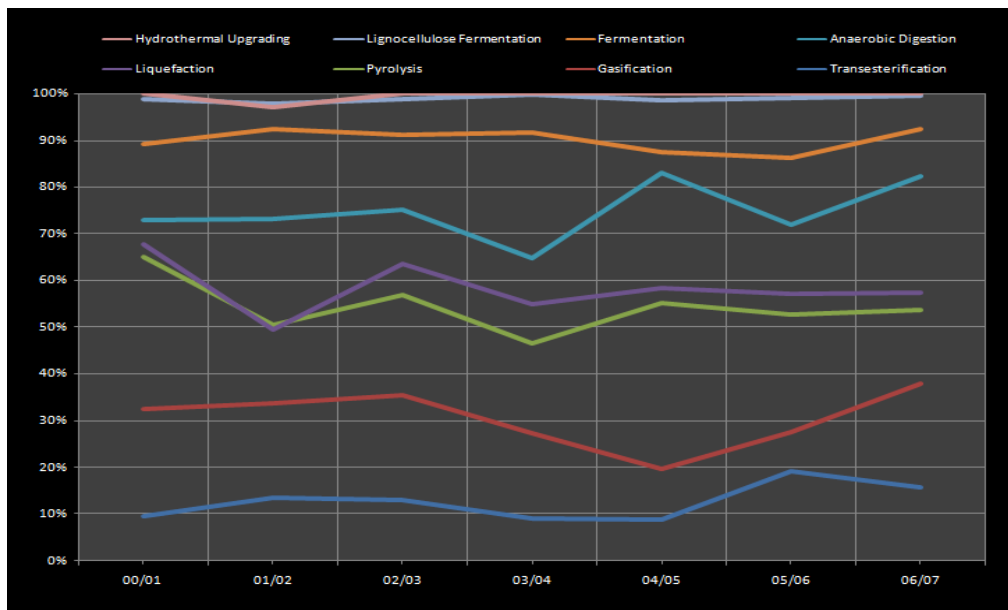


Figure 24. Acceleration rate of the publications number on each technology research since 1995 (data obtained using Google Scholar)

The acceleration rate curve allows better understanding of the evolution patterns. It can be seen that lignocellulosic fermentation and gasification are the technologies with higher positive slope, which means each year the increase in the publications number is higher than the year before. This may be explained by their potential, but also based on the fact that these technologies have remaining challenges to overcome, before becoming commercially viable. The only technology that presents a negative slope is the oil conversion through transesterification.

A third graph with annual cumulative number of publication is available in appendix 5, as well as the already presented figures 23 and 24, for a better visualization.

3.7 Case-study: Microalgae Fuels

3.7.1 Biomass Characterization

Microalgae are microscopic, simple, aquatic plants typically found in freshwater and marine habitats. They are mainly composed of carbohydrates, proteins and plant oil.

As microalgae grow they capture solar energy and CO_2 in their photosynthetic system. They are the simplest and most primitive plants, but also the most efficient converters of solar energy as they can use up to 10% of the solar energy. They also have higher grow-rates, can grow in conditions not favourable for most of the terrestrial plants, and have triglyceride production rates 45-220 times higher than terrestrial biomass (Huber et al., 2006).

Figure 25 presents a description of some microalgae composition, and in appendix 6 it is possible to analyse an old research on chemical composition of various microalgae families.

As it can be observed in figure 25, the microalgae containing higher lipid content, within the selected, is *Botryococcus Braunii*. The microalgae with higher protein percentage are *Isochrysis sp.*, and the higher carbohydrate content is present in *Dunaliella bardawil*.

species	growth conditions		organic component (dry wt %)					
	NaCl level (molar)	nutrients	ash	lipid (triglyceride)	protein	carbohydrate	glycerol	unknown
<i>Botryococcus braunii</i>	0	enriched	5.6	44.5	22.0	14.1	0.1	19.3
	0	deficient	7.8	54.2	20.6	14.3	0.1	10.8
	0.5	enriched	59.6	46.3	15.0	13.3	0.1	25.3
<i>Dunaliella bardawil</i>	2.0	deficient	14.7	10.4	9.7	40.4	16.4	23.1
<i>Dunaliella salina</i>	0.5	enriched	8.6	25.3	29.3	16.3	9.4	19.7
	0.5	deficient	7.7	9.2	12.5	55.5	4.7	18.1
	2.0	enriched	21.7	18.5	35.9	12.5	27.7	5.4
<i>Ankistrodesmus sp.</i>	0	enriched	4.5	24.5	31.1	10.8	0.1	33.5
<i>Isochrysis sp.</i>	0.5	enriched	12.0	7.1	37.0	11.2	0.1	44.6
	0.5	deficient	52.0	26.0	23.3	20.5	0.1	30.1
	1.0	enriched	65.9	15.3	34.7	15.5	0.1	34.4
<i>Nannochloris sp.</i>	0	enriched	13.6	20.8	33.1	13.2	0.1	32.8
<i>Nitzschia sp.</i>	1.4	enriched	20.4	12.1	16.8	9.2	0.1	61.8

Figure 25. Composition of microalgae species as dry weight % grows under different conditions (Huber et al., 2006)

Another study, focusing in microalgae oil content, is presented in figure 26, where it can be observed that like *Botryococcus Braunii*, others species of microalgae have enormous oil contents.

Microalga	Oil content (% dry wt)
<i>Botryococcus braunii</i>	25–75
<i>Chlorella sp.</i>	28–32
<i>Cryptocodinium cohnii</i>	20
<i>Cylindrotheca sp.</i>	16–37
<i>Dunaliella primolecta</i>	23
<i>Isochrysis sp.</i>	25–33
<i>Monallanthus salina</i>	>20
<i>Nannochloris sp.</i>	20–35
<i>Nannochloropsis sp.</i>	31–68
<i>Neochloris oleoabundans</i>	35–54
<i>Nitzschia sp.</i>	45–47
<i>Phaeodactylum tricornutum</i>	20–30
<i>Schizochytrium sp.</i>	50–77
<i>Tetraselmis sueica</i>	15–23

Figure 26. Oil content of some microalgae species (Chisti, 2007)

3.7.2 Technical Evaluation of the Technology

As mentioned, microalgae need CO₂ and solar energy to their grown, but they also need great amounts of water and inorganic salts. These nutrients must be provided by the growth medium, including normally nitrogen (N), phosphorus (P), iron and in some cases silicon. The minimal nutritional necessary feed can be estimated by the approximate molecular formula of microalgae: CO_{0.48}H_{1.83}N_{0.11}P_{0.01} (Chisti, 2007). A promising method of providing water to microalgae may involve the

use of waste water, supplying the microalgae with some nutrients and treating the water at the same time (Carlsson et al., 2007).

Microalgae are commercially produced in photobioreactors or in raceway open ponds. In raceway open ponds there are almost no control under variables like temperature, nutrients concentration and water evaporation, they occupy a larger area than photobioreactors and have normally poisoning problems associated. However, they are normally extremely cheaper to install and to operate. Photobioreactors are normally arrays of straight transparent tubes or opaque tanks with incorporated sources of light. They allow an extremely efficient control over variables and minimize the poisoning, allowing single species growing optimization.

When they reach their maximum grow rate, they are ready to be processed. This process begins with water removal, which is recycled to the bioreactor. The microalgae biomass is then processed to biofuels production. This system is presented in figure 27.

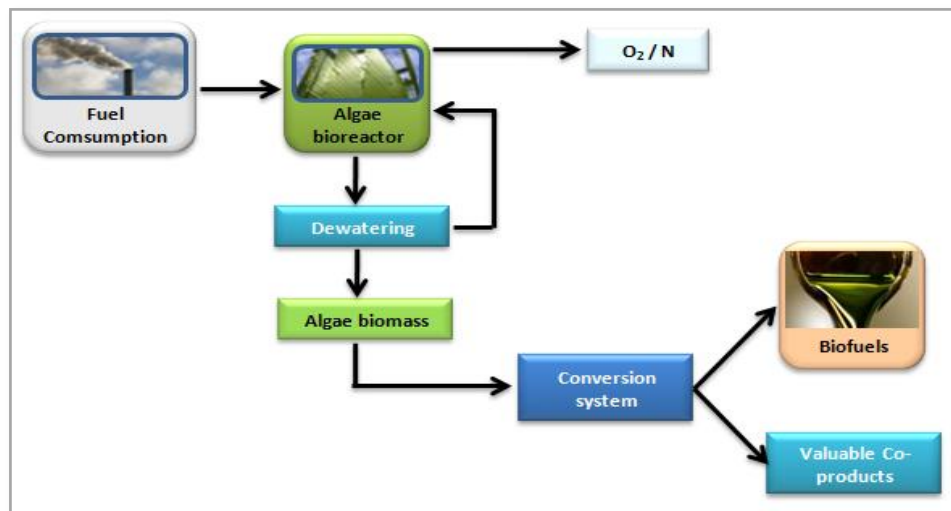


Figure 27. Microalgae conversion system flow diagram

The way microalgae biomass is processed to biofuel production, depends on the biofuel that is to be produced but essentially of the chemical composition of the algal biomass. Figure 28 presents the available options. All the presented processes are explained in appendix 1.

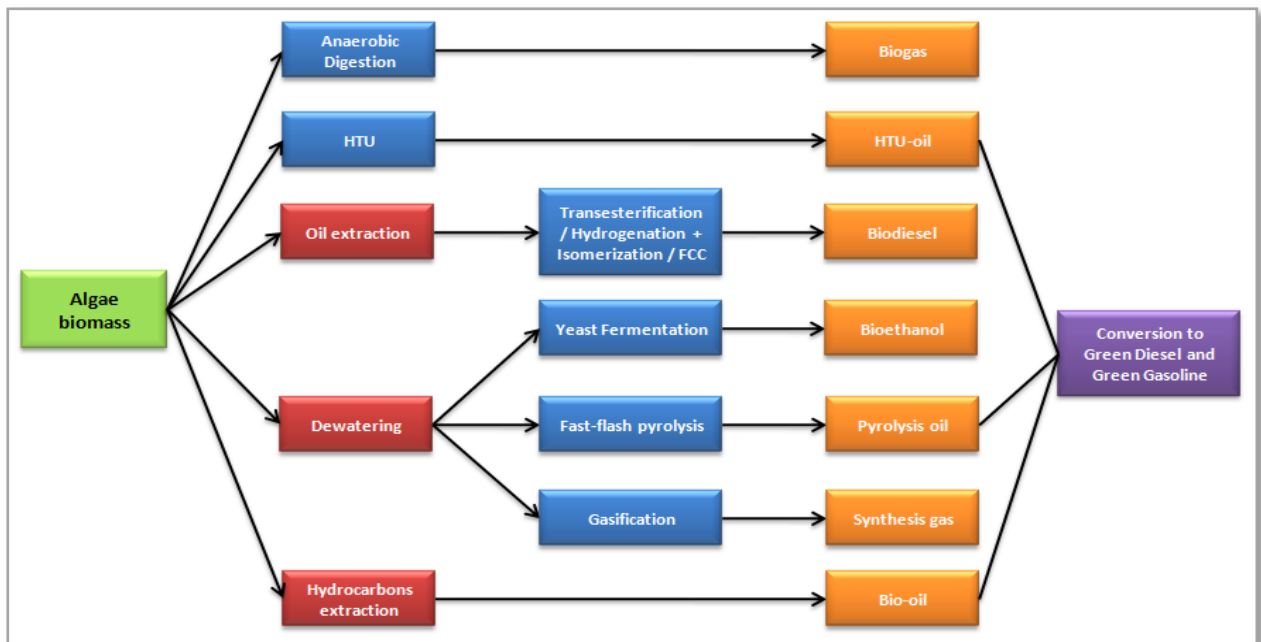


Figure 28. Possibilities for conversion of microalgae biomass to biofuel

If the microalgae have a higher level of lipids, they are more appropriate for biodiesel production. Higher starches content is more suitable for fermentation into ethanol. Sometimes the use of process that may perform with wet biomass may become more economically viable, face to the processes for dry biomass, as no pre-treatment process is necessary like dewatering and oil extraction (Harmelen & Onk, 2006).

Harvesting and dewatering

The first step in this diagram is the harvesting. This can be accomplished through many processes:

- chemical flocculation
- froth flotation
- bioflocculation
- microstraining
- membrane filtration
- centrifugation
- ultrasounds

Chemical flocculation uses chemicals like alum and ferric chloride, and chitosin (commercial product) to perform the flocculation. However, this method is too expensive for large operations. In froth flotation the water and microalgae are aerated into froth. In bioflocculation the microalgae essentially harvest themselves by first flocculating (single cells aggregating) and then sinking to form a dense mass. Microstraining is basically the harvest with backwashed 25-50 µm mesh rotating screens. Both

bioflocculation and microstraining allow a small dewatering, as the final slurry has 3-5% of solid matter. For certain conversion processes, further dewatering may be necessary. The choice of the harvesting method also depends on the species, on cell density, and often on the culture conditions (Carlsson et al., 2007).

In processes like anaerobic digestion and HTU a light dewatering, or even no dewatering may apply because they allow biomass with high moisture content. For yeast fermentation, fast-flash pyrolysis and gasification, low moisture or dry biomass is necessary. When the process to perform is fermentation, first a light dewatering may be necessary, for a more efficient hydrolysis and subsequent conversion. For the biodiesel production route, another important step is necessary: the oil extraction. The oil extraction methods and their explanation may be consulted in appendix 1.

In this process where an extraction is necessary, the algal residues may be applied as fertilizers, may be burned to electrical energy production, may be used to provide new nutrients on the photobioreactor, or may even pass through anaerobic digestion for SNG production.

Microalgae that produce hydrocarbons

Another pathway for biofuel achievement is the direct production of hydrocarbons through microalgae (last route on figure 28). A very explored example is *Botryococcus Braunii*. In this case the algal biomass is constituted of a mixture of hydrocarbon, kind of an “algal crude”, that can be converted to green fuels or direct used in the engine, like occurs with bio-oil and HTU-oil. This is one of the most promising features of microalgae biofuels.

A recent approach for turning economically viable the microalgae conversion system is the biorefinery concept. This concept is related to, within other issues explained in section 3.8, the valorisation of the conversion by producing high-value co-products. In the microalgae case many co-product may be produced since this market is not new. Examples of this co-products are small molecules like iodine, algin, mannitol and L-fraction, polymers, hydrocolloids, ulvan (group of polymers), pharmaceuticals and cosmetics, high value oil, colourants, and many others (Carlsson et al., 2007).

3.8 Biorefinery

The bio-refinery concept is related to process biomass into biofuels, combined with the manufacture of high added-value materials and chemicals, and other forms of energy such as heat and electricity. It has a great potential such as an efficient and cost-effective way of producing biofuels, and may allow overcoming the problems founded on reaching an economically viable production of biofuels (Ruiz, 2005). These biorefineries integrate various conversion processes and make better use of waste materials to produce a range of products including fuels, industrial chemicals, heat and electricity (The

Royal Society, Jan 2008). All the conversion processes routes may be included: biochemical, thermochemical and physicochemical, to extract maximum value. Several commercial and pilot plants are already functional in bioethanol production, such as BRI in Arkansas, Ornskoldsvik in Sweden and logen in Canada, but also in wood processing through gasification and FT synthesis, such as Güssing in Austria, Värnamo in Sweden and Choren in Germany. An interesting approach is the idea of developing a virgin wood-based biofuel biorefinery incorporated into an existing pulp mill (Pu et al., 2007).

A study on biorefinery concept for The Netherlands, proposes the use of flash pyrolysis (figure 29), which is already being developed in a BTG demo plant (Malaysia), as a single process or integrated one in a biorefinery. This propose stands in the fact that flash pyrolysis and the subsequent treatment of oil, gas and solid fractions obtained, may produce a wide variety of fuels and valuable co-products (Annevelink et al., 2006).

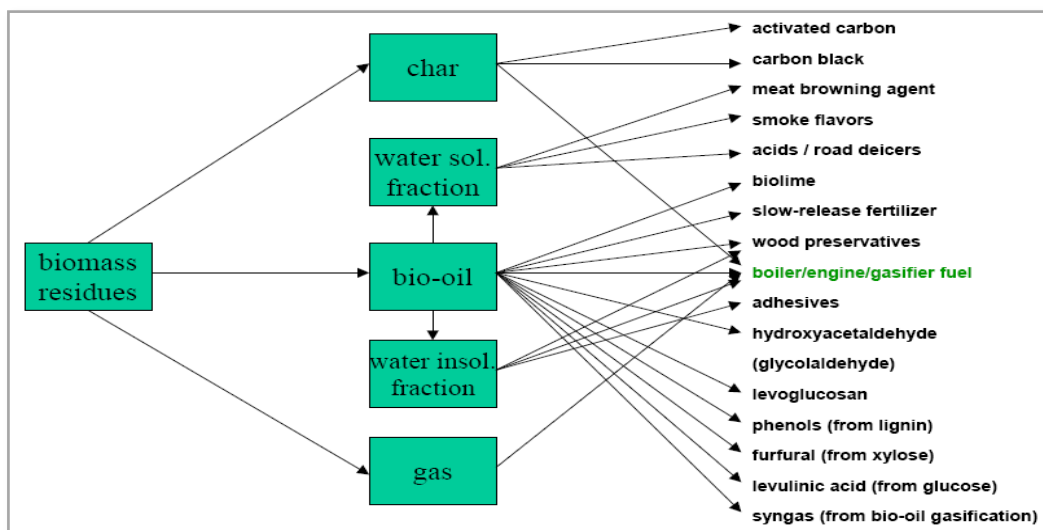


Figure 29. Fast Pyrolysis for fuels and co-products in biorefinery concept

3.8.1 Microalgae based biorefinery flow diagram

The following scheme represents what could be a near term biorefinery for microalgae main feed, optimized for liquid biofuels production.

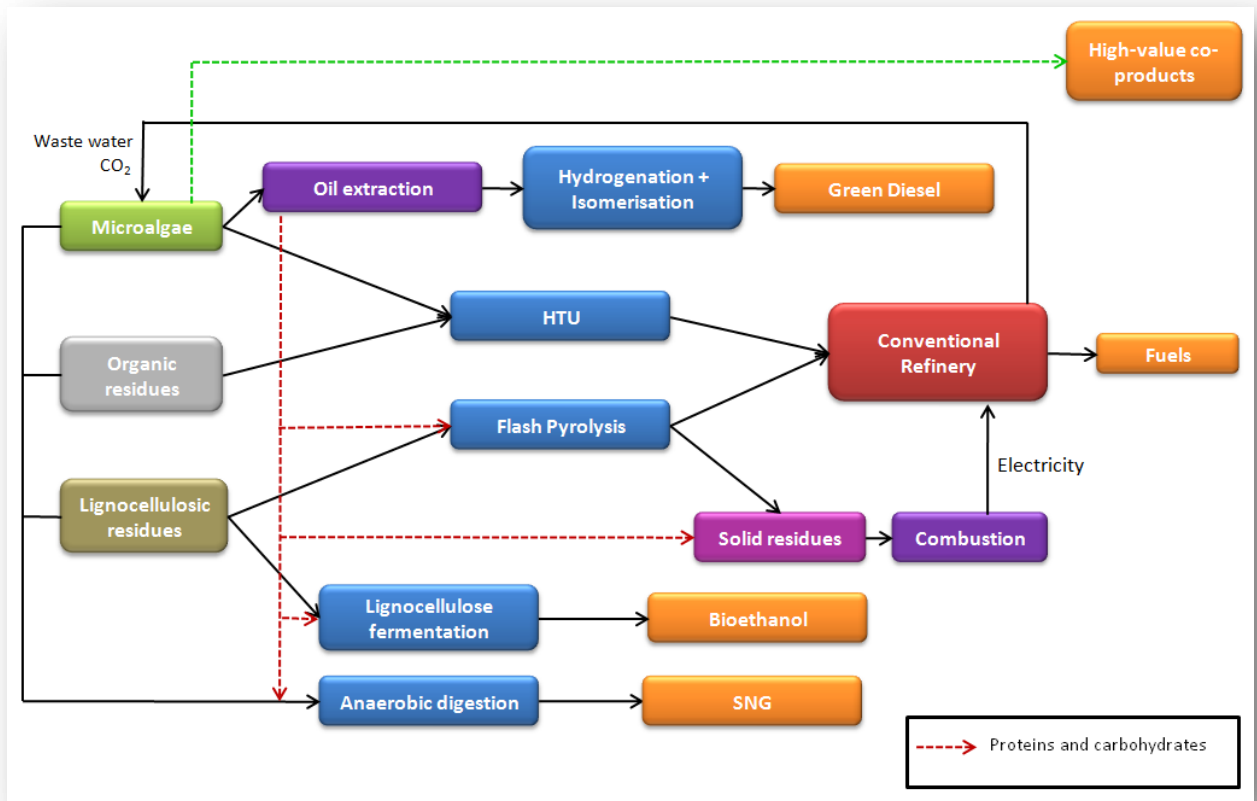


Figure 30. Biorefinery concept within this work (microalgae as main feed)

As most of the microalgae have several compounds such as oil, carbohydrates, proteins, among others, a biorefinery concept may be the ideal solution for maximizing the whole biomass potential. As it can be observed in the flow diagram, the microalgae may be converted into biodiesel after the oil extraction, or converted to HTU-oil. Biodiesel production may be preferred if the alga has high oil content, or if an economic and energetic assessment proves that it brings more advantages. In this case, oil is converted to biodiesel, and the residues may be used for HTU-oil production or for production of electricity, SNG and bioethanol. In case the assessment indicates no economic and energetic advantages in this pathway, converting all microalgae through HTU may be the best option. As referred earlier, additional other high-value products may be obtained from microalgae.

Waste treatment represents nowadays a major problem for many countries. The integration of this biomass type in a biorefinery feed may solve this problem, and allow the production of fuels and co-products. Forest biomass utilization has the same advantages, as the forest residues collection may prevent the huge number of fires in our country.

4 Conclusions

Regarding to engine performance, the main conclusions of this study are that alcohols, biogas and biodiesel can be used as motor fuels either as blending components or as is. Alcohols and gaseous fuels are suitable for spark-ignited engines, whereas vegetable oil and animal fat derivatives are suitable for diesel engines. Synthetic fuels as green diesel, HTU diesel and green gasoline, resemble current fuel qualities and can be used in existing vehicles without modifications. The current production technologies for synthetic fuels emphasize diesel type products.

The economic assessment allowed concluding that bioethanol from lignocellulosic and FT diesel are the biofuels with highest price values. However, it was also possible to verify that there was great discrepancy between the estimates given by the different research works. For the investment costs on the various technologies, the highest values correspond to lignocellulosic biomass fermentation, and to conversion of synthesis gas into CH₄ (SNG) and methanol. The lowest values are for conversion of synthesis gas to Fischer-Tropsch synthetic diesel and gasoline, sugar fermentation and PVO from oil extraction.

As for the evolution analysis, most technologies for biofuel production have already passed from lab-scale to pilot plants, and many others have been scaled-up. Biomass-to-Liquid technologies are the most advanced in the pilot plant phase, followed by lignocellulosic bioethanol.

The biomass resources that currently represent the higher potential are lignocellulosic biomass, microalgae, *Jatropha curcas* and kudzu. Biomass like organic waste from industry and households is a biomass resource which is expected to increase in importance as a source for bioenergy with a stronger emphasis towards recirculation. Many researchers are trying to solve biomass current limitations, such as efficiency on solar energy capture, higher energetic final products production, and especially trying to solve lignocellulosic biomass limitations, focusing on GEO.

There is a research project to produce “microdiesel”, where oil are converted through transesterification, but the process avoids the use of methanol, because instead scientists engineered a specific form of *Escherichia coli* bacterium, so once the modified *E. coli* is allowed to work on the vegetable oil, it produces its own ethanol which acts as a substitute for the toxic methanol. There are also research projects focus in developing microalgae that efficiently produce hydrogen, named “hydrogen micro-factories”, GEO that allow the rise the metabolic efficiency of microalgae to increase their biofuels capacity production, as high lipid content. The tendency is that the development of biotechnology and genomics tools will enable the development of crops with specific traits that are optimized for biofuels.

A bibliometric study in section 3.6 indicates that lignocellulosic fermentation and gasification for subsequent biofuels production are the technologies that present a higher increase in research number.

All the issues related to biofuels and presented in this report, as environmental impact, production costs, final fuel price, energy content, competition with food, biodiversity threatening, social well-being, engine performance, among others, may influence the development trends of biofuels technologies, but the economic and energetic balance will certainly be the most influent.

It is also possible to conclude that for choosing the most suitable microalgae biomass conversion processes, attention must be focus on their chemical properties, as they will hardly influence the final product. As most of the microalgae have several compounds such as oil, carbohydrates, proteins, among others, a biorefinery concept may be the ideal solution for maximizing the whole biomass potential.

The microalgae may be converted into a diesel type fuel after the oil extraction, or converted to HTU-oil. Biodiesel production may be preferred if the microalgae has high oil content, or if an economic and energetic assessment proves that it brings more advantages. In this case, oil is converted to biodiesel, and the residues may be used for HTU-oil production or for production of electricity, SNG and bioethanol. The conversion of this oil into biodiesel may be achieved through transesterification or by hydrotreatment producing a synthetic diesel. However the hydrotreatment process seems to be the most promising. This process consists of mixing oil fractions with hydrogen in the presence of a catalyst, which under determined operational conditions produces specified diesel, is gaining importance throughout the world. Even being a catalytic process, under severe operational conditions (high temperatures and pressures) and which consumes hydrogen, the advantages obtained with this refining technology outweigh the costs, allowing better use of heavy loads, improved product quality and environmental protection by removing pollutants such as sulfur and nitrogen. The synthetic diesel (green diesel) produce through HDT has also the advantage of being capable to be used up to 100% concentration in conventional engines.

Higher starches content is more suitable for fermentation into ethanol. Sometimes the use of process that may perform with wet biomass may become more economically viable, face to the processes for dry biomass, as no pre-treatment process is necessary like dewatering and oil extraction

In case the assessment indicates no economic and energetic advantages in this pathway, converting all microalgae through HTU may be the best option. Beyond this additional other high-value products may be obtained from microalgae.

The future biomass conversion technologies future may pass through genetically modify microalgae to better solar energy conversion. The most promising conversion route may be hydrotreatment to produce green diesel, HTU-oil production or bio-oil production through flash pyrolysis, oils that can be further used directly in fuel engines, or can be incorporated as feed for conventional refineries, and that allow the production of a diesel type fuel with properties very similar to the conventional diesel.

5 Evaluation of the Performed Work

5.1 Achieved Goals

The major goal of the present study was to formulate and substantiate an opportunity map of the present and future technologies, for its use on the conversion of different types of biomass to biofuels. The main purpose relies on the fact that to accurately plan a strategy for biofuels production it is necessary to fully understand the currently available options for biofuels production

The proposed goals were achieved through an intensive literary search on the biomass conversion processes, which implies identifying the main biomass types and biofuels possible to obtain - inputs and outputs identification. Once identified the relevant and present conversion routes it was possible to perform an economic comparison between them through the available literature data. The initial objective of determine the total investment and operations costs for all technologies was not possible to fulfil, because the majority of the technologies are not in a commercial scale, and the project data and suitable equipment were not already identified. It was also an objective identifying the evolution trends and patterns based on evolution assessment methods such as (Rantanen & Domb, 2002) and Philomemetic, and through literature data and a bibliometric assessment. The application of TRIZ and Philomemetic became less relevant face to the data obtained from literature, so they were not performed.

Finally, the second goal of this report is to perform two case-studies: identifying the most suitable and recent options for microalgae biomass conversion, and developing a biorefinery concept where the main feed corresponds to microalgae biomass.

5.2 Other Works Completed

Beyond the already referred means to fulfil the proposed goals, it was considered relevant to identify the important and most accurate papers based on the subject. The same was done to identify the most relevant players on the current biofuels production market and R&D.

5.3 Limitations and Future Work

A more detailed economic assessment would be interesting, but it would only be applicable for a more specific situation, with a small number of technologies to assess and well defined inputs and outputs.

6. References

- Adam, J. (2006). Possibilities for conversion of biomass to liquid fuels in Norway - background information for a roadmap. *SINTEF Biomass Seminar*. Oslo.
- Aden, A. (2007). *Biomass and Biofuels: Technology and Economic Overview*. Maryland, EUA: NREL.
- Annevelink, E., Jong, E. d., Ree, R. V., & Zwart, R. (2006). *First Workshop on the possibilities of biorefinery concepts for the industry*. The Netherlands: WUR and ECN.
- Aresta, M., Dibenedetto, A., & Barberio, G. (2005). *Utilization of macro-algae for enhanced CO₂ fixation and biofuels production: Development of a computing software for a LCA study*. Italy: Elsevier.
- Ashworth, J. (2006). *From Biomass to Biofuels - NREL leads the way*. EUA: NREL.
- Balat, M. (2008, Jan 01). Mechanisms of Thermochemical Biomass Conversion Processes Part 1: Reactions of Pyrolysis. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* .
- Balat, M. (2008b, Jan 01). Mechanisms of Thermochemical Biomass Conversion Processes. Part 2: Reactions of Gasification. *Energy Sources Part A: Recovery, Utilization, and Environmental Effects* .
- Biodieselbr Online. (09 May 2008). Portugal: Fábricas de biodiesel procuram novas alternativas de negócio. *BiodieselBR* .
- BMELV, GTZ & FNR. (2006). *Biofuels For Transportation*. Washington: BMELV.
- Carlsson, A. S., Beilen, J. B., Möller, R., & Clayton, D. (2007). *Micro- and Macro-algae: utility for industrial applications*. UK: CPL press.
- Chakinala, A. (2007). *Supercritical water gasification of biomass*. The Netherlands: University of Twente.
- Chisti, Y. (2007, February 13). Biodiesel from microalgae. *Science Direct* .
- Crutzen, P. J. (2007). N₂O release from agro-biofuel production negates global warming reduction by replacing fossil fuels. *Atmos. Chem. Phys. Discuss.* , p. 7(4).
- Demirbas, A. (2006). Progress and recent trends in biofuels. *Progress in Energy and Combustion Science* 33 (2007) 1-18 .
- Demirbas, M. F. (2006, September 01). Current Technologies for Biomass Conversion into Chemicals and Fuels. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* , pp. 1181-1188.
- DENA. (2006). *Biomass to Liquid - BtL - Implementation Report*. Berlin, Germany: German Energy Agency.
- Dupain, X., Costa, D. J., Schaverien, C. J., Makkee, M., & Moulijn, J. A. (2007). Cracking of a rapeseed vegetable oil under realistic FCC conditions. *Applied Catalysts. B, Environmental - Vol. 72* , pp. 44-61.
- Eikeland, O. (2006). *Biofuels- the new oil for thr petroleum industry?* Norway: Fridtjof Nansens Institutt.
- EU Biofuels Technology Platform. (2008). *Strategic Research Agenda & Strategy Deployment Document*. UK: CPL Press.

- EU Intelligent Energy - Program Refuel. (2008). *Eyes on the track, Mind on the horizon - From inconvenient rapeseed to clean wood: A European road map for biofuels*. EU Communities.
- Ezeji, T. C., Qureshi, N., & Blaschek, H. P. (2007, June). Bioproduction of butanol from biomass: from genes to bioreactors. *Current Opinion in Biotechnology - Vol. 18, Issue 3* , pp. 220-227.
- Faaij, A. (2006). *Modern biomass conversion technologies*. The Netherlands.
- Goudriaan, F., Naber, J., & Berg, E. v. (2006). *Conversion Of Biomass Residues To Transportation Fuels With The HTU Process*. Alkmaar: Biofuel B. V. / HVC Groep.
- GTZ. (2005). *Synopsis of Greman and European experience and state of the art of biofuels for transport*. Germany.
- Hall, N., & Taylor, C. (2006). *Emerging supply-side energy technologies*. PB Power.
- Hamelinck, C. N. (2004). *Outlook for advanced biofuels*. The Netherlands.
- Harmelen, T. V., & Oonk, H. (2006). *Microalgae biofixation processes: applications and potential contributions to greenhouse gas mitigation options*. Italy: Eni Technologie.
- Harmsen, R. (2008). *Energy Supply Chain: Biofuels*. Ecofys Academy.
- Hastbacka, M. A. (2005). Biomass Conversion: From Concept to Commercialization, Part 1. *Technology Management Journal* .
- Heilbron, I. M. (1941). *Somes aspects of algal chemistry*.
- Houghton, J., Weatherwax, S., & Ferrel, J. (2006). *Breaking the biological barriers to cellulosic ethanol*. USA: U. S. Department of Energy.
- Huber, G. W. (2008). *Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels: Next Generation Hydrocarbon Biorefineries*. Washington D.C.: University of Massachusetts Amherst.
- Huber, G. W., Iborra, S., & Corma, A. (2006, Feb 3). Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts and Engineering. *Chemical Reviews* , 106, pp. 4044-4098.
- Huber, G. W., O'Connor, P., & Corma, A. (2007). *Processing biomass in conventional oil refineries: Production of high quality diesel by hydrotreating vegetable oils in heavy vaccum oil mixtures*. The Netherlands: Science Direct.
- Huntley, M. E., & Redalje, D. G. (2007). CO2 mitigation and renewable oil from photosynthetic microbes: A new appraisal. *Mitigation Adaptation Strategies Global Change* , p. 12(4).
- Innovative Natural Resource Solutions LLC. (2006). *Maine Department of Economics & Community Development - Office of Innovation*. Portland.
- International Energy Agency. (n.d.). http://www.iea.org/Textbase/stats/pdf_graphs/PTTPESPI.pdf. Retrieved April 8, 2008, from www.iea.org.
- Jacquot, J. (2008, June 15). Newsweek interview: Craig Venter's CO2-Eating Miracle Bacterium. *Science & Technology* .

-
- Jungmeier, G. (2008). Environmental Aspects of the Biofuels for Transport in Europe. *Biomass & Bioenergy Confenrece 2008*. Estonia Fair Center, Tallinn, Estonia: JOANNEUM RESEARCH, Austria.
 - Kalnes, T., Marker, T., & Shonnard, D. R. (2007). Green diesel: A Second Generation Biofuel. *International Journal of Chemical Reactor Engineering* , 5 (Paper on UOP/Eni Ecofining process).
 - Kalscheuer, R., & Stölting, T. (2006). *Microdiesel - Biodiesel Production from Bacteria*. Germany.
 - Kampman, B. E., Boer, L. C., & Croezen, H. J. (2005). *Biofuels under development*. The Netherlands: CE Solutions for Environment, Economy and Technology.
 - Karlsson, M. (2007). *Sustainable Bioenergy: A framework for Decision Makers*. United Nations: UN-Energy.
 - Kavalov, B., & Peteves, S. D. (2005). *Status and perspectives of biomass-to-liquid fuels in the European Union*. European Commission. Petten, The Netherlands: Institute for Energy.
 - Kimes, L., & Perla, D. (Dez 2007). *Biomass Conversion: Emerging Technologies, Feedstocks and Products*. Washington: EPA - United States Environmental Protection Agency.
 - Koppejan, J. (2004). Crude oil from biomass with the HTU process. *EMIMENT Workshop 8-9/March*. Riga: TNO Environment, Energy and Process Innovation.
 - Koskinen, P. (2005). *H2 Production in fluidized-bed bioreactor through dark fermentation*. Tampere University of Technology.
 - Lange, J.-P. (2007, July 18). Lignocellulose conversion: an introduction to chemistry, process and economics. *Biofuels, Bioproducts & Biorefining* , p. 45.
 - Larsen, H., & Petersen, L. (2007, November). Future options for energy technologies. *Risø Energy Report*
 - Larsen, H., Kossmann, J., & Petersen, L. S. (2003). *Riso Energy Report 2*. New and emerging Technologies, National Laboratory for Sustainable Energy, Technical University of Denmark - DTU, Roskilde, Denmark.
 - Larson, E. D. (2008). *Biofuel production technologies: status, prospects and implications for trade and development*. Geneva: United Nations.
 - Lewis, N. S., & Nocera, D. G. (2006). *Powering the planet: Chemical challenges in solar utilization*. USA: Proc. Natl. Acad. Sci.
 - Londo, H. M., Lensink, S. M., Deurwaarder, E. P., & Wakker, A. (2008). *Biofuels cost developments in the EU27+ until 2030*. REFUEL WP4 final report, ECN Policy Studies, REFUEL.
 - MacDonald, T. (2007). *Alcohol Fuels from Biomass - Assessment of Production Technologies*. Western Governor's Association.
 - Makinën, T., & McKeough, P. (2005). *Biofuture - Final Project Report*. Finland: VTT Processes.
 - Malhotra, R. K. (2007, Jan). Road to emerging alternatives- Biofuels and Hydrogen. (D. J. Lal, Ed.) *Journal of the Petrotech Society, Volume IV, No.1* .
 - McKendry, P. (2001, July 06). Energy production from biomass (part 2): conversion technologies. *Bioresource Technology* 83 .

-
- McLaren, J. S. (2005). Crop biotechnology provides an opportunity to develop a sustainable future. *Trends in Biotechnology* , 23, 339-342.
 - Neto, F., & Rosa, F. (2001). Energias Renováveis em Portugal. FORUM “Energias Renováveis em Portugal”. Lisboa: ADENE / INETI.
 - Nylund, N.-O., Saksa, P. A., & Sipilä, K. (2008). *Status and outlook for biofuels, other alternative fuels and new vehicles*. Finland: VTT Technical Research Centre of Finland.
 - Østergård, H. (2007). *Bioenergy and emerging biomass conversion technologies*. Germany: Risø National Laboratory.
 - Pu, Y., Zhang, D., Singh, P., & Ragauskas, A. J. (2007, November 12). The new forestry biofuels sector. *Biofuels, Bioproducts & Biorefining* , 2, pp. 58-73.
 - Quirin, M., & Gärtner, S. (2004). *CO2 mitigation through biofuels in the transport sector*. Germany: IFEU.
 - Rantanen, K., & Domb, E. (2002). *Simplified TRIZ - New problem-solving applications for engineers and manufacturing professionals*. St. Lucie Press.
 - Rosa, M. F. (2006). *Situação actual dos biocombustíveis e perspectivas futuras*. INETI, Departamento de Energias Renováveis. Gazeta de Física.
 - Ruiz, P. F. (2005). Editorial. *RENEW - Renewable Energy Newsletter* , Issue 3.
 - Rutz, D., & Janssen, R. (2007). *Biofuel Technology Handbook*. Germany: WIP RENEwable Energies.
 - Schenk, P. M., Thomas-Hall, S. R., Stephens, E., Marx, U. C., Mussnug, J. H., Posten, C., et al. (2008). *Second Generation Biofuels: High-Efficiency Microalgae for Biodiesel Production*. Australia: Springer Science.
 - Sharpe, V. J. (2008, April / May). Revolutionizing Biofuels With Emerging Technologies. *BBI Biofuels Canada* .
 - Subramani, V., & Gangwal, S. K. (2007). *A Review of Recent Literature to Search for an Efficient Catalytic Process for the Conversion of Syngas to Ethanol*. USA: ACS Publications.
 - The Royal Society. (Jan 2008). *Sustainable biofuels: prospects and challenges*. UK: The Clyvedon Press Ltd.
 - Thuijl, E. V., Roos, C. J., & Beurskens, L. W. (2003). *An overview of biofuel technologies, markets and policies in Europe*. Energy research Centre of the Netherlands. Amsterdam, The Netherlands: ECN.
 - UN-Energy. (Apr 2007). *Sustainable bionenergy: a framework for decision makers*. United Nations.
 - US Department of Energy. (2002). *Roadmap for Biomass Technologies in the United States*.
 - Vessia, O. (2005). *Biofuels from lignocellulosic material - In the Norwegian context 2010 - Technology, Potencial and Costs*. Norway: NTNU.
 - Wright, M. M., & Brown, R. C. (2008, April 14). Distributed processing of biomass to bio-oil for subsequent production of Fischer-Tropsch liquids. *Biofuels, Bioproducts & Biorefining* , p. 232.

Appendix 1 Processes description

In this appendix is presented a detailed description of the processes included in the *Biomass Conversion Map*.

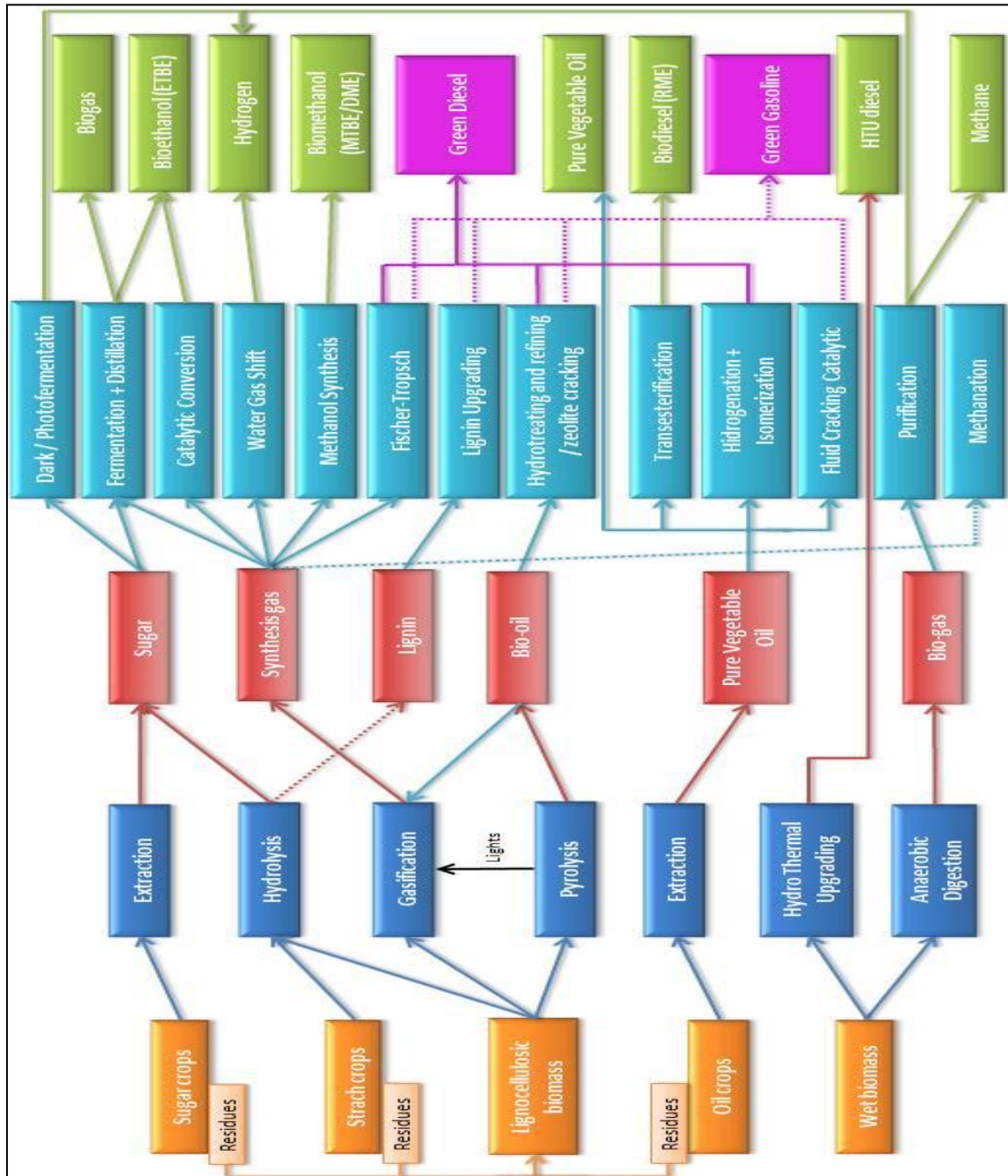


Figure 31. Biomass Conversion Map

1.1 Fermentation routes and Lignin Upgrading

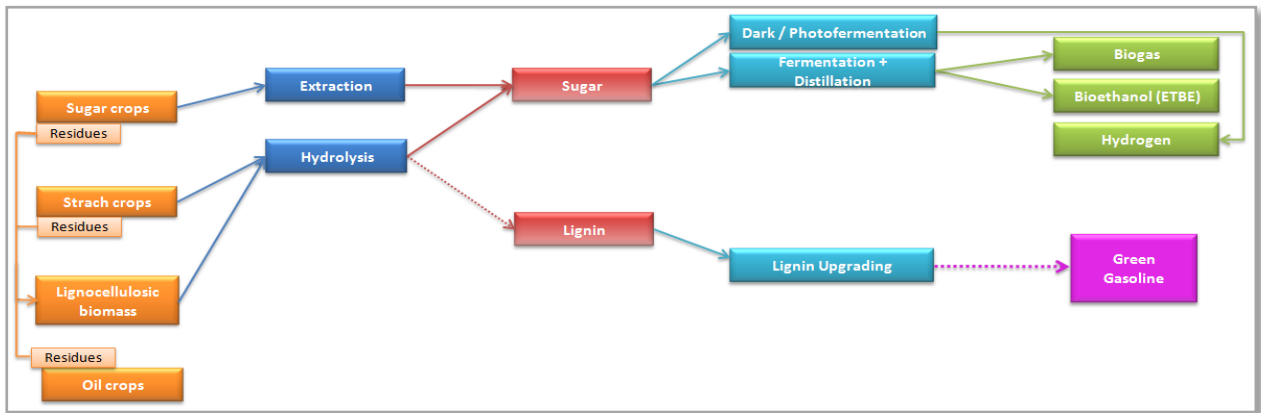


Figure 32. Part of the Biomass Conversion Map (part 1)

Extraction

When sugar exists naturally in certain crops, they can be released by a simple extraction procedure that includes milling, shearing, gridding or extruding (MacDonald, 2007) and washing with hot water to release the sugar from the plant material. This is necessary because before the fermentation step (whether is dark, photo or normal fermentation), a treatment process may be performed to remove plant material, chemical substances or wild microorganisms that could inhibit the fermentation process.

The pathway from lignocellulose to the final products includes a hydrolysis step because cellulose must be first converted to sugars before can be converted to ethanol, followed by fermentation. Another similar way of conducting this is through Simultaneous saccharification and fermentation (SSF) (Adam, 2006). Both alternatives are better illustrated in figure 33.

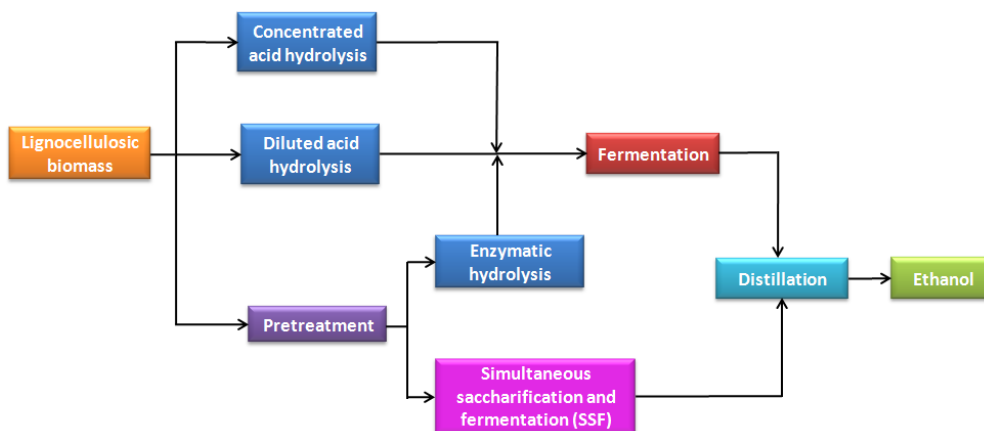


Figure 33. Detailed lignocellulose routes of conversion - adapted from (Adam, 2006)

Hydrolysis

Hydrolysis of cellulose or starch is usually called as saccharification. The process consists on breaking the cellulose, hemicellulose and starch part of the biomass and converting it into fermentable sugars. Actually three types of hydrolysis are possible: acid hydrolysis (dilute acid or concentrated acid hydrolysis) and enzymatic hydrolysis are presented in figure 33, the third type not presented is alkaline hydrolysis. In either option, the material must be initially processed to reduce size and facilitate its handling, and then acids or enzymes are used to break apart or hydrolyze the hemicellulose and cellulose chains to form their monomeric sugars (MacDonald, 2007). If enzymes are used, a pre-treatment step is necessary to render the cellulose fraction accessible to the cellulose enzymes complex.

Diluted acid hydrolysis usually occurs in two stages to take advantage of the differences there are between cellulose and hemicellulose. The first involves low temperature to maximize the yield from the hemicellulose, and the second with higher temperature to perform the same with cellulose fraction. It is normally performed with less than 1% sulphuric acid solution, breaking down the hemicellulose into its component sugars (xylose and others) (MacDonald, 2007).

Concentrated acid hydrolysis normally is preceded by a diluted acid pre-treatment to separate the hemicellulose and cellulose. Then, after the concentrated acid perform, water is added to dilute and heated to release the sugars, producing a gel that can be separated from residual solids (MacDonald, 2007).

A method of reducing costs in the diluted and concentrated acid hydrolysis is to perform it as countercurrent hydrolysis (MacDonald, 2007). This approach runs on two stages: feedstock is introduced to a horizontal co-current reactor with a conveyor, than steam is added to raise the temperature o 180 °C, without acid, and exit the reactor when 60 % of the hemicellulose is hydrolysed. On the second stage it enters on a vertical reactor operated at 225 °C, where is feed a very diluted acid and almost all the remaining hemicellulose is hydrolysed.

Enzymatic hydrolysis is very similar to the previous processes, but the acid is replaced by enzyme cellulase to break the chains of the remaining sugars (cellulose) to release glucose. As the cellulase enzymes can be used at lower temperatures, 30 to 50 °C, it reduces the sugars degradation (MacDonald, 2007).

Pre-treatment

The pre-treatment step is necessary when the hydrolysis step will be realized through enzymes. The objective is to alter the structure of biomass in order to make the cellulose and hemicellulose more

accessible and amenable to hydrolytic enzymes that can generate fermentable sugars (Pu et al., 2007). Many options of pre-treatment are available:

- Mechanical (grinding, milling, shearing, extruding)
- Acid treatment (dilute or concentrated sulphuric acid)
- Alkali treatment (sodium hydroxide, ammonia, alkaline peroxide)
- Autohydrolysis (steam pressure, steam explosion, liquid hot water)
- Organic solvent treatment (ethanol/water, acetone/water)

Fermentation

Commercial fermentation is usually realized in batch and temperature-controlled tanks. Initially the sugars are mixed with water forming a broth, than this broth is adjusted to meet the needs of the microorganisms changing the sugar concentration, and nutrients such as a nitrogen source are added to facilitate the reactions. Still before the fermentation the temperature is brought to the optimum value, and the fermentation begins as the growing population of microorganisms produces enzymes to break two-molecule sugars into single molecule sugars, and then convert these into the commercial chemicals or by-products. Yields of chemicals approach a limit as the microorganisms either consume all the fermentable sugars or the products and by-products of fermentation inhibit the organism (Huber et al., 2006).

Dark/Photofermentation

This fermentation process uses bacteria to process organic matter and water into hydrogen. As the name indicates, photofermentation requires light and dark fermentation does not need a light source (Koskinen, 2005).

Distillation

The products from fermentation are a mixture of ethanol, cell mass and water. As the microorganisms do not allow for high concentrations of ethanol, a first step separating the ethanol from the diluted solution in a distillation column is necessary, where water remains with the solids. Then, to perform a further increase on the ethanol concentration, another distillation may be applied, or by using molecular sieves (Vessia, 2005).

Simultaneous Saccharification and Fermentation (SSF)

In this process cellulase and fermenting yeast are combined, so that as sugars are produced the fermentative organisms convert them to ethanol in the same step. This process is an attractive method for keeping monomeric sugars such as glucose at low enough concentrations to avoid enzyme inhibition

(Pu et al., 2007). In this process, although the temperature of the SSF process is lower than the optimal temperature for enzymatic hydrolysis, because the fermentation organisms are not stable at these higher temperatures, the rates, concentrations and yields are better than for separated hydrolysis and fermentation (Adam, 2006).

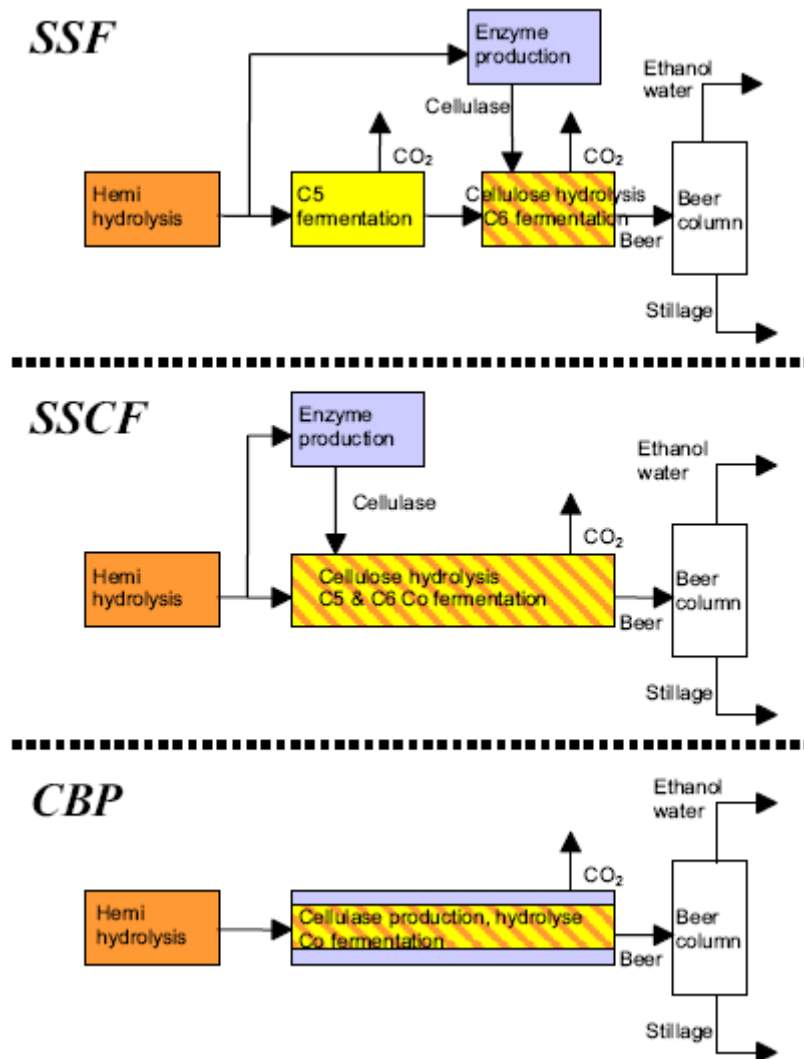


Figure 34. Options for bioethanol production through hydrolysis and fermentation (Hamelinck, 2004)

Simultaneous Saccharification and Co-Fermentation (SSCF)

A process similar to SSF, where the number of necessary reactors is reduced to two, because it allows hydrolysis and fermentation of both sugar types. In this process cellulase and fermenting yeast for C5 and C6 sugars are combined in the same reactor (Vessia, 2005).

Consolidated Bio-Processing (CBP)

In this technology, ethanol and all the required enzymes are produced by a single microorganism community, in a single reactor. It is not necessary an external reactor for the enzyme production, lowering the operational and equipment costs (Pu et al., 2007).

Lignin Upgrading

Lignin upgrading may be achieved by a catalytic process, because to convert it into a product compatible with the transportation fuel market it has to decrease its molecular weight (Huber et al., 2006).

1.2 Gasification and Pyrolysis routes

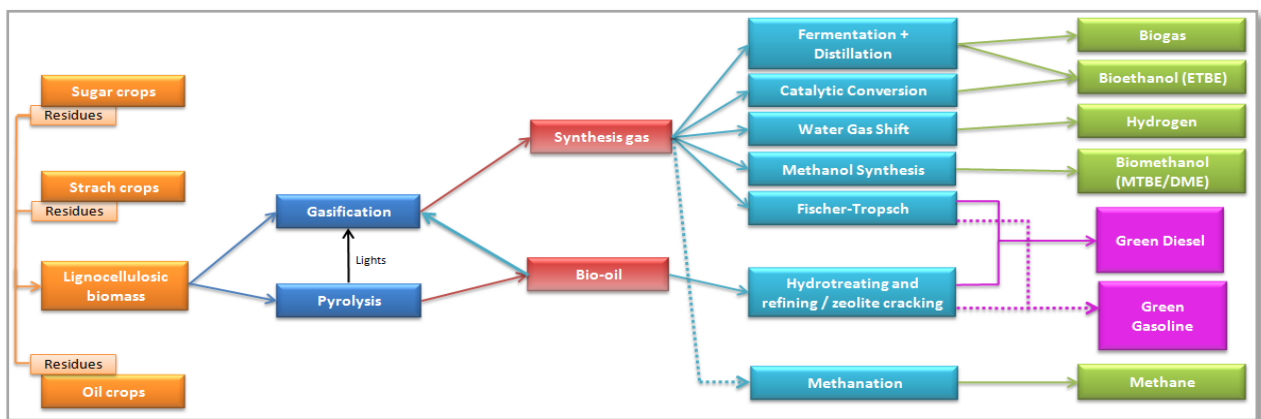


Figure 35. Part of the Biomass Conversion Map (part 2)

The presented route of biomass gasification to synthesis gas, and further liquefaction of this gas to biofuels is a technology known as Biomass-to-Liquid (BTL), which has been extensively researched.

Gasification

Gasification is a thermochemical decomposition process through which biomass is converted to a gaseous state (85%) by oxidation in the limited presence of oxygen, at high temperatures - typically in the range of 800-1000 °C, under 20-30 bar and with long residence times (Balat, 2008b). The formed gas is a mixture of carbon monoxide and hydrogen called synthesis gas or syngas. This process has been achieved through a wide range of designs for the gasification chamber. As an alternative to this thermal treatment, pyrolysis plasma has been recently developed to yield a syngas stream. (The Royal Society, Jan 2008)

Fermentation of synthesis gas

A type of application of synthesis gas is conversion through organisms to produce bioethanol. This is achieved by the anaerobic bacterium *clostridium ljungdahlii*. The reactor fermentation vessels are constructed with the aim of short retention time (Adam, 2006).

Catalytic conversion

After gasification a catalytic conversion may be applied to syngas in order to produce bioethanol and hydrogen. Homogeneous and heterogeneous catalytic processes are available, but homogeneous catalytic processes are relatively more selective for ethanol (Subramani & Gangwal, 2007).

Water Gas Shift (WGS)

In this process the carbon monoxide reacts with water to form hydrogen and CO₂. Industrially this is achieved in two series of reactors: a first a high temperature WGS reactor at 350-500 °C with a Fe-oxide-based catalyst and a second low temperature WGS reactor at around 200 °C with a Cu-based catalyst. (Huber et al., 2006)

Methanol Synthesis

Methanol synthesis reaction from synthesis gas is normally performed with Cu/ZnO-based catalyst (Demirbas, 2006) at 220-300 °C and 50-100 bar. This synthesis is a combination of two exothermic reactions, the WGS reaction and hydrogenation of CO₂ to methanol. There are now catalysed conversion processes capable of converting methanol to green gasoline and diesel. Conversion to green gasoline is performed by MTG (Methanol to Gasoline) and the conversion to green diesel by MOGD (Methanol to Olefins, Gasoline and Diesel) (The Royal Society, Jan 2008).

Fischer-Tropsch

Is a catalysed thermochemical reaction where carbon monoxide and hydrogen created by gasification of feedstock are converted into hydrocarbons. This process has the potential to create hydrocarbons from C1 to C50, but with the right control over temperature, pressure and catalyst it is possible to control the range and distribution of the products. With this control it is possible to create synthetic transport fuels such as green gasoline and green diesel, with exactly the same properties as fossil fuels derived fuels. (Huber et al., 2006)

Methanation

Methanation is a catalysed process that converts synthesis gas (mainly carbon monoxide and hydrogen) into CH₄ with a nickel-based catalyst. The aim of this CH₄ formation is normally the production of Synthetic Natural Gas (SNG), usually called bio-SNG or green gas. (The Royal Society, Jan 2008)

Pyrolysis

Pyrolysis is a thermochemical process that performs the conversion of biomass to a liquid (termed bio-oil or bio-crude), solid and gaseous fractions, by heating the biomass in the absence of air and at a temperature around 500°C (Balat, 2008). The categorization of this process depends on the temperature value and on the residence time (Demirbas, 2006). Slow pyrolysis uses low temperatures and long residence time, conditions that maximize the yield of char. Fast pyrolysis is the most favourable technology when the objective is to obtain liquid biofuels as it maximizes the bio-oil production (75%) using high heating rates, moderate temperatures (500 °C) and very short residence times. Examples of this approach are vacuum pyrolysis and flash pyrolysis (Adam, 2006).

Bio-oils are complex mixtures of oxygenated hydrocarbons, water and char particles. They have to be upgraded if they are to be used as a replacement for diesel and gasoline fuels, because among other reasons presented in section 3.4, they normally present low heating value and high viscosity. Three possible processes of upgrading it to have properties similar to conventional fuels are hydro-deoxygenation, zeolite cracking and fermentation. The first to produce green diesel and fermentation produces bioethanol. To use it as blend for conventional fuels it can be simply deoxygenated.

Hydro-deoxygenation (HDO)

This process involves treating bio-oils at moderated temperatures (300-600 °C) with high pressure hydrogen in the presence of heterogeneous catalysts. During HDO the oxygen in the bio-oil reacts with the hydrogen to form water and saturated C-C bonds. (Huber et al., 2006)

Zeolite Cracking

Bio-oil can be upgraded using zeolite catalysts to reduce oxygen content and improve thermal stability. Temperatures of 350-500 °C and atmospheric pressure are used. During this process a number of reactions occur including dehydration, cracking, polymerization, deoxygenation and aromatization. (Huber et al., 2006)

Bio-oil Fermentation

In this process the anhydrosugar and carbohydrates parts of the bio-oil are fermented to produce ethanol and water. (Huber, 2008)

Conversion of bio-oil by gasification

This route appeared because it can be largely advantageous to convert the biomass into bio-oil through pyrolysis near to the place where it is collected, and then transport it to perform the gasification, than transport the solid biomass. Synthesis gas can be produced from bio-oil through a catalytically steam-gasification at relatively low temperatures, with total destruction of tar. (Huber, 2008)

Another possibility to convert bio-oil into synthesis gas is Steam Reforming. This process occurs at high temperature (600-800 °C) and high space velocities usually with a Ni-based catalyst. (Huber, 2008)

1.3 Oil crops and wet biomass conversion

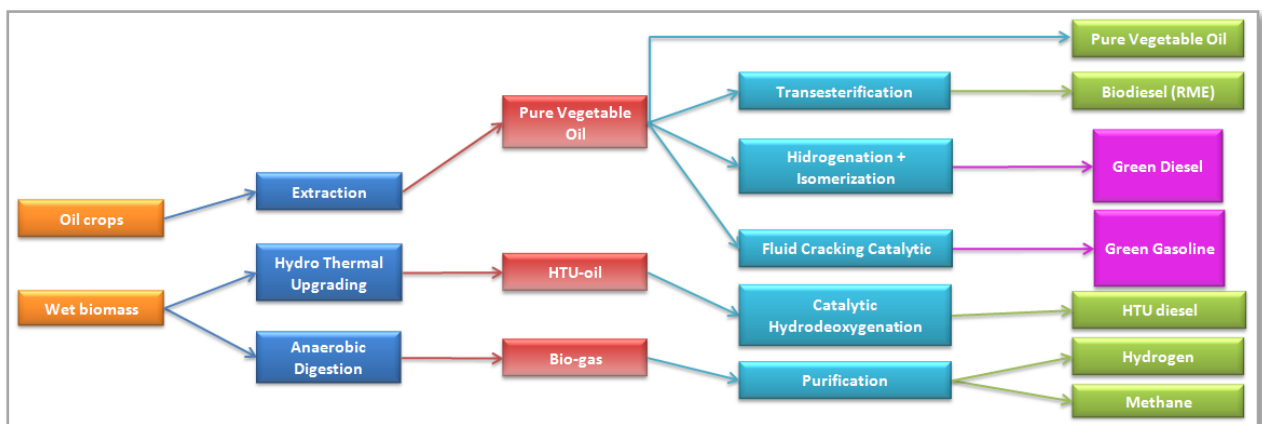


Figure 36. Part of the Biomass Conversion Map (part 3)

Extraction

Before oil can be converted into biofuels or utilized simply as pure vegetable oil (PVO), it has to be extracted from the oil seed. This process may be achieved by mechanical press extraction or by organic solvent extraction where the desired lipid compounds are dissolved in the solvent for later separation (Aresta et al., 2005). The most recent alternative approaches are:

- supercritical fluid extraction
- enzymatic extraction

-
- aqueous enzymatic extraction
 - osmotic shock
 - sonification (ultrasonic extraction)
 - microwave extraction
 - steam explosion (flashing water into steam through rapidly increasing temperature or pressure)
 - extraction through pressurization

Pure Vegetable Oil conversion:

Transesterification

Transesterification is the reaction of triglycerides (or other esters) with alcohols to produce alkyl esters (biodiesel) and glycerol, typically in the presence of acid or base catalysts. Methanol, due to its low cost, is the alcohol most commonly used, although other alcohols such as ethanol and 2-propanol can produce biodiesel with better fuel characteristics. This process both reduces the viscosity of the fatty acids and converts them to a combustible form. There are several methods for carrying out this reaction without a catalyst, such as supercritical process, ultrasonic process and even microwave process. Esterification is a pre-treatment process sometimes necessary to prepare the fatty acids for transesterification. (Huber et al., 2006)

Hydrogenation and Isomerisation

Vegetable oil can be hydrotreated to produce straight chains alkanes ranging from C₁₂ to C₁₈. The conditions are 350-450 °C and 40-150 atm with conventional hydrotreating catalysts (sulphided NiMo/Al₂O₃). The reaction pathway involves hydrogenation of the C=C bonds of the vegetable oils, followed by alkane production by three different pathways: decarbonylation, decarboxylation and hydrodeoxygenation. The straight chain alkanes pass then through isomerisation and cracking to produce green diesel (Huber et al., 2007).

Another approach for vegetable oil conversion, not presented in the *Biomass Conversion Map*, is pyrolysis and zeolite upgrading. Vegetable oils can also be pyrolysed to produce a liquid fuel that contains linear and cyclic paraffins, olefins, aldehydes, ketones and carboxylic acids. This reaction may be done with or without a catalyst. Zeolite upgrading is a nonselective process making a range of compounds and undesired coke and lighter alkanes. (Huber et al, 2006)

Fluid Cracking Catalytic

Process that works through catalysts, high temperature and moderate pressure to convert the vegetable oils to gasoline-range hydrocarbons that are low in sulphur and nitrogen content. The high

aromatization of the fatty acids causes the formation of large amounts of aromatics in the gasoline fractions. (Dupain et al., 2007)

Wet biomass can be converted to high valuable fuels by hydro thermal upgrading, anaerobic digestion and supercritical water gasification. The great advantage of process that can process biomass with high moisture contents is that any of the presented biomass types in the *Biomass Conversion Map* can be included in this category, so it means that it is possible to join all the biomass resources and convert it through the same process.

Hydro Thermal Upgrading (HTU)

This is a thermochemical process also called pressure liquefaction where wet biomass can be converted by treatment in liquid water, at temperatures between 300 and 350 °C and pressures from 100 to 180 bar, conditions that represent sub (near) critical water (Goudriaan et al., 2006). It is very similar to fast pyrolysis but processes wet biomass and produces a bio-oil, HTU-oil, with 15-20 % of oxygen content (compared with 35-40 % with pyrolysis) (The Royal Society, Jan 2008). This HTU-oil can be further pass through Catalytic Hydrodeoxygenation and produce a diesel-type fuel called HTU-diesel. As the feedstock is wet biomass, a broad range of feedstocks can be converted such as sugar crops, lignocellulosic biomass, oil crops and organic waste (Goudriaan et al., 2006).

Anaerobic Digestion

Is a biochemical process through which high moisture content biomass can be consumed by bacteria in an anaerobic environment (without oxygen), and converted to a gas named biogas, a mixture of mainly CH₄ (50-55 %), CO₂ and small quantities of other gases (The Royal Society, Jan 2008). By the removal of CO₂ the biogas may be upgraded to higher quality synthetic natural gas (SNG). Sources of biogas include landfill sites and large scale digesters for municipal solid waste or marine biomass. (McKendry, 2001)

Supercritical Water Gasification (SWG)

At supercritical conditions water behaves like an adjustable solvent and has adjustable properties depending on the temperature and pressure. Biomass gets rapidly decomposed and the cleavage products of the biomass dissolve in the supercritical water there by minimizing the tar and coke formation. This technology seems to be very promising for the production of energy rich gases like hydrogen, synthesis gas and CH₄ (for SNG) from the wet biomass (Chakinala, 2007). Synthesis gas can be then converted through all the processes presented in the *Biomass Conversion Map*.

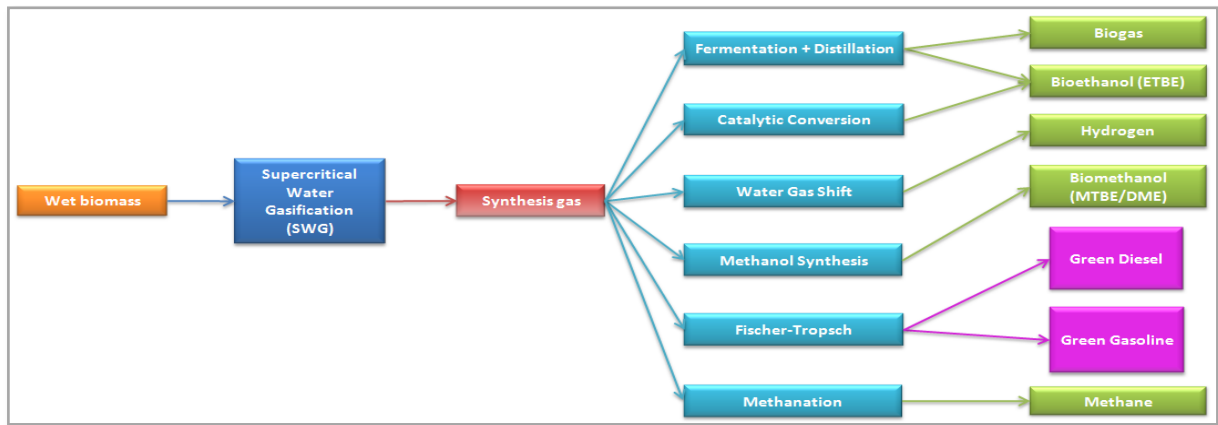


Figure 37. Supercritical water gasification pathway

Appendix 2 GHG emissions and energy balance

The following figure expresses the biofuels GHG emissions balance and the energy balance in terms of avoidance costs - costs per avoided primary energy source demand or avoided GHG emissions, i.e. earned capital on substituting fossil fuels for biofuels, expressed in € for CO₂ ton saved or by € for GJ saved.

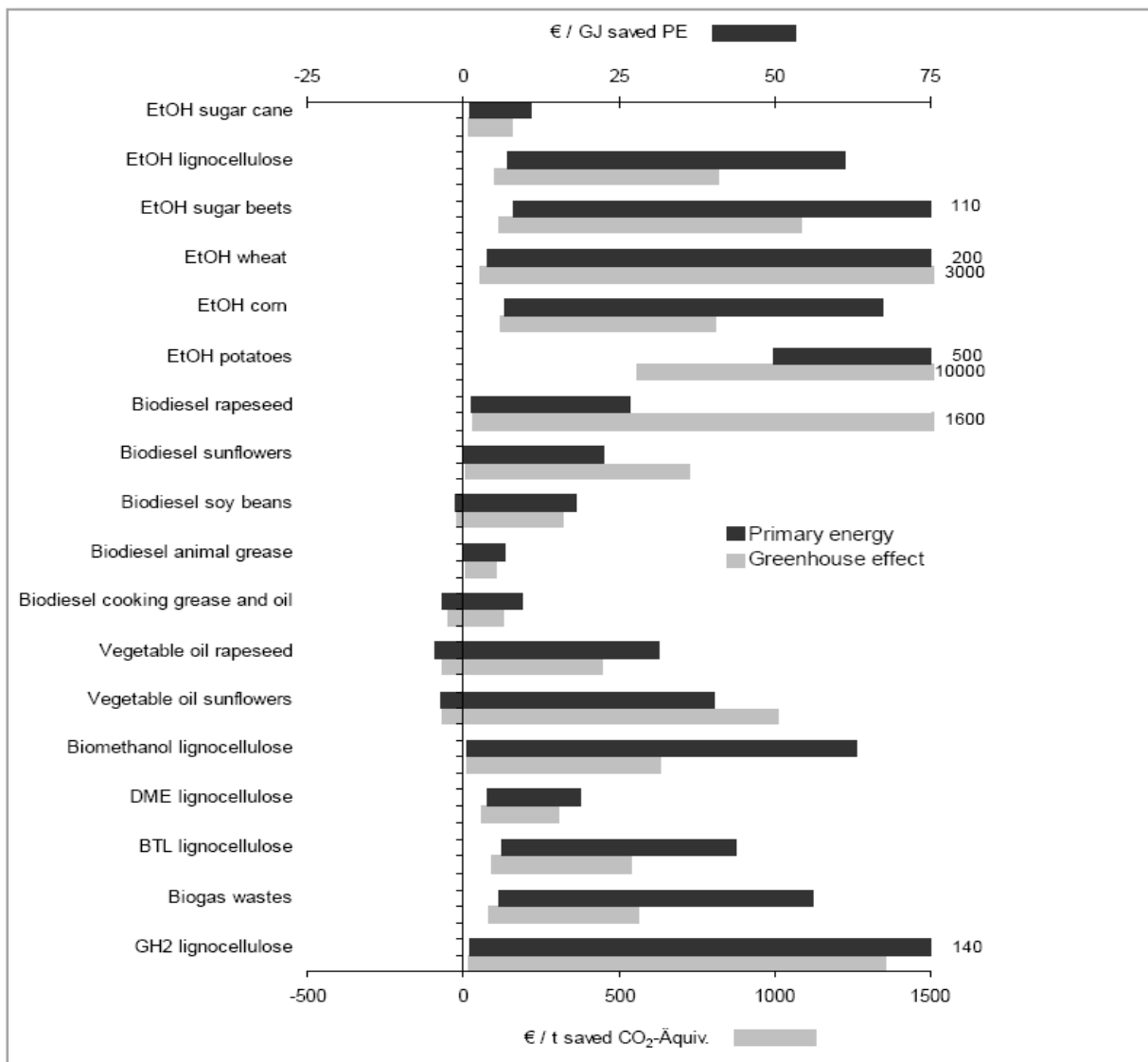


Figure 38. Costs per saved primary energy source consumption or GHG emissions in €/GJ saved non-renewable primary energy or €/ton saved CO₂ equivalent [GH2 - gaseous hydrogen; EtOH - ethanol] (Quirin & Gärtner, 2004)

Appendix 3 Economic data

3.1 Economic studies of the technologies

Gasification + FT		Fast Pyrolysis	
	Cost (millions)		Cost (millions)
Pre-treatment	\$71.6	Handling and drying	\$5.57
Gasifier	\$61.4	Pyrolysis reactor	\$3.92
Oxygen plant	\$51.1	Quench	\$1.94
Cleaning section	\$61.4	Heat recovery	\$1.14
Shift	\$3.41	Product recovery and storage	\$0.80
F-T reactor	\$20.5	Recycle	\$1.38
Gas turbine	\$23.9	Steam and power production	\$3.16
Heat recovery steam generator	\$37.5	Utilities	\$3.13
Other	\$10.2	Contingency	\$7.37
Total	\$341	Total	\$28.4

^a Only total capital costs employed in scaling calculations.

Figure 39. Capital cost components of gasification to Fischer-Tropsch liquids and fast pyrolysis plants (Wright & Brown, 2008)

Concept	Investment costs (Euro/kWth input capacity)		O&M (% of inv.)	Estimated production costs (Euro/G,J fuel)	
	Short term	Long term		Shorter term	Longer term
Hydrogen: via biomass gasification and subsequent syngas processing. Combined fuel and power production possible; for production of liquid hydrogen additional electricity use should be taken into account.	480 (+ 48 for liquefying)	360 (+ 33 for liquefying)	4	9-12	4-8
Methanol: via biomass gasification and subsequent syngas processing. Combined fuel and power production possible	690	530	4	10-15	6-8
Fischer-Tropsch liquids: via biomass gasification and subsequent syngas processing. Combined fuel and power production possible	720	540	4	12-17	7-9
Ethanol from wood: production takes place via hydrolysis techniques and subsequent fermentation and includes integrated electricity production of unprocessed components.	350	180	6	12-17	5-7
Ethanol from beet sugar: production via fermentation; some additional energy inputs are needed for distillation.	290	170	5	25-35	20-30
Ethanol from sugar cane: production via cane crushing and fermentation and power generation from the bagasse. Mill size, advanced power generation and optimised energy efficiency and distillation can reduce costs further on longer term.	100 (wide range applied depending on scale and technology applied)	230 (higher costs due to more advanced equipment)	2	8-12	7-8
Biodiesel RME: takes places via extraction (pressing) and subsequent esterification. Methanol is an energy input. For the total system it is assumed that surpluses of straw are used for power production.	150 (+ 450 for power generation from straw)	110 (+ 250 for power generation from straw)	5 4	25-40	20-30

Figure 40. Global overview of current and projected performance data for the main conversion routes of biomass to fuels (Faaij, 2006)

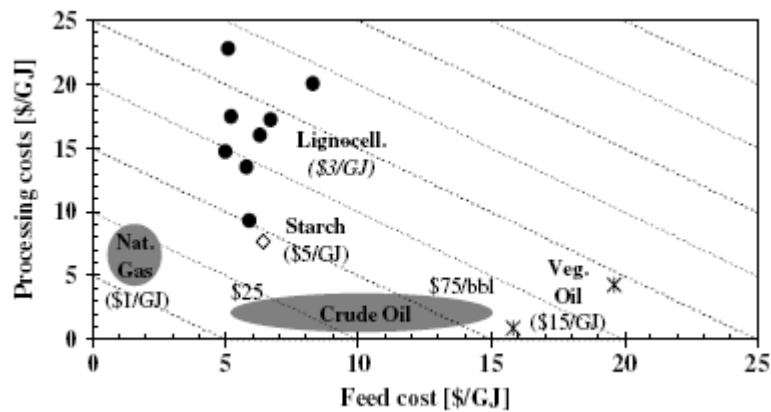


Figure 41. Feed and processing cost of transportation fuels derived from lignocellulose and fossil resources (the biofuel plants are set at 400 MW intake, which corresponds to <680 kt/a of lignocellulose) (Lange, 2007)

3.2 Studies on biofuels prices comparison

Biofuel	2006 (US cents/litre)	Long-term about 2030 (US cents/litre)
1 Price of oil, US\$/barrel	50–80	
2 Corresponding pre-tax price of petroleum products US cents/litre	35–60	
3 Corresponding price of petroleum products with taxes included, US cents/litre (retail price)	150–200 in Europe About 80 in USA	
4 Ethanol from sugar cane	25–50	25–35
5 Ethanol from corn	60–80	35–55
6 Ethanol from beet	60–80	40–60
7 Ethanol from wheat	70–95	45–65
8 Ethanol from lignocellulose	80–110	25–65
9 Bio-diesel from animal fats	40–55	40–50
10 Bio-diesel from vegetable oils	70–100	40–75
11 Fischer-Tropsch synthesis liquids	90–110	70–85

Note: the estimates for the biofuels and Fischer-Tropsch liquids are rounded (adapted from IEA 2006).
 (a) note range differs from row 1, for several factors such as refinery costs.
 (b) Excluding a few outliers above and below this range.

Figure 42. Estimated costs of biofuels compared with the prices of oil and oil products (The Royal Society, Jan 2008)

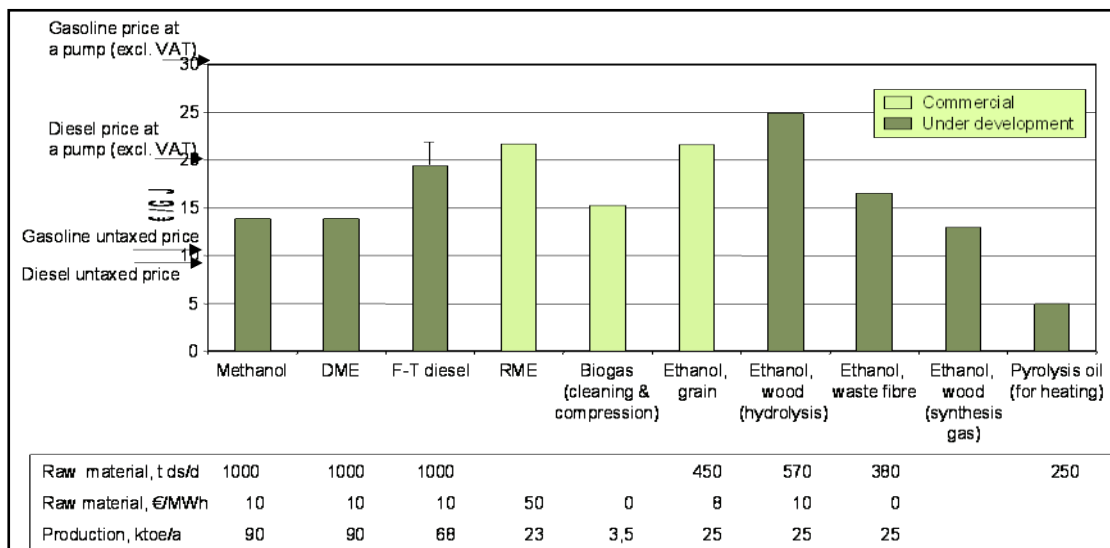


Figure 43. Production cost levels of some biofuels for transportation [source: ethanol from wood via syngas by NREL, The USA] (Makinen & McKeough, 2005)

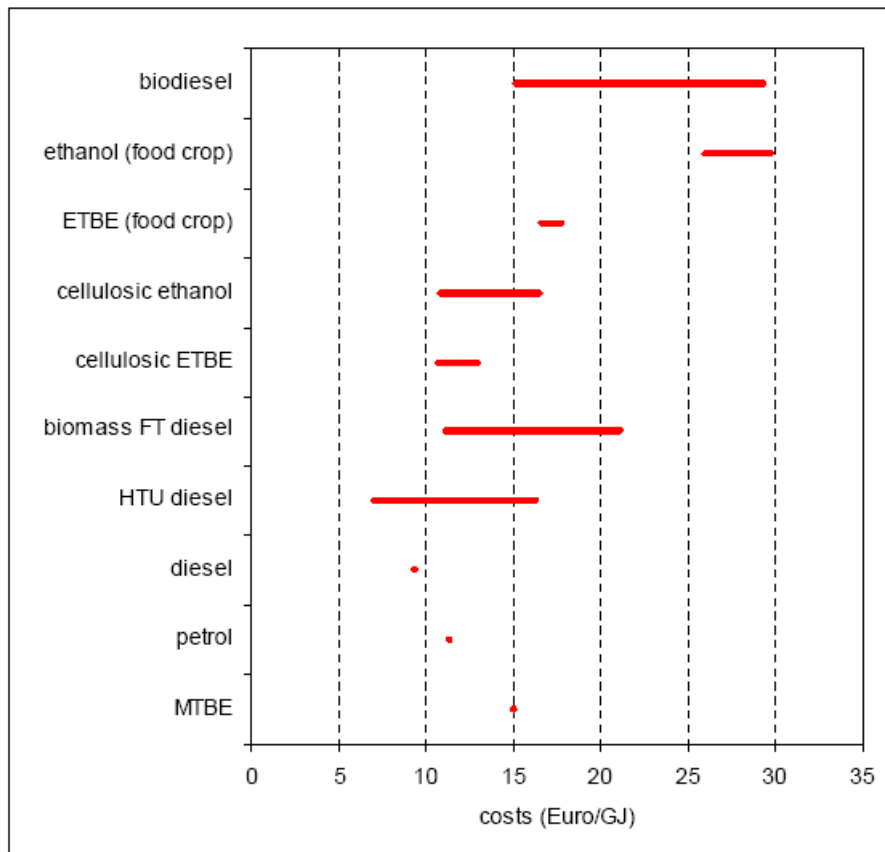


Figure 44. Cost estimates of the various biofuels, compared with the average cost of diesel and petrol in 2002-2004 (Kampman et al., 2005)

Table 3. Biofuels prices estimates by several researches

Biofuel	Biomass resource	Process	Price	Unit	Source
Biodiesel	Lignocellulose	Gasification + FT synthesis	0,49	€/L	(DENA, 2006)
Biodiesel	Tallow	Transesterification	0,31-0,50	€/L	(Hall & Taylor, 2006) / IEA
Biodiesel	Rapeseed	Transesterification	0,49-0,95	€/L	(Kampman, Boer & Croezen, 2005)
Biodiesel (present)	Rapeseed	Transesterification	0,5	€/L	(Thuijl, Roos & Beurskens, 2003)
Biodiesel (long term)	Rapeseed	Transesterification	0,2	€/L	(Thuijl, Roos & Beurskens, 2003)
Bioethanol	Dry Corn	Simultaneous Saccharification & Co-Fermentation	0,18	€/L	(Aden, 2007)
Bioethanol	Putrescible waste	Enzymatic Hydrolysis + Fermentation	0,38-0,79	€/L	(Hall & Taylor, 2006) / EECA
Bioethanol	Lignocellulose	Gasification + Methanol synthesis	0,19	€/L	(MacDonald, 2007)
Bioethanol	Lignocellulose	Hydrolysis + Fermentation	0,37	€/L	(MacDonald, 2007)
Bioethanol	Lignocellulose	Hydrolysis + Fermentation	0,11-0,32	€/L	(Thuijl, Roos & Beurskens, 2003)
Bioethanol	Lignocellulose	Hydrolysis + Fermentation	0,27	€/L	(Thuijl, Roos & Beurskens, 2003) / NREL
Bioethanol (present)	Sugar & Starch	Hydrolysis + Fermentation	0,32-0,54	€/L	(Thuijl, Roos & Beurskens, 2003)
Bioethanol (long term)	Lignocellulose	Hydrolysis + Fermentation	0,24	€/L	(Hall & Taylor, 2006) / IEA
Bioethanol (long term)	Lignocellulose	Hydrolysis + Fermentation	0,23	€/L	(Kampman, Boer & Croezen, 2005)
Bioethanol (near term)	Lignocellulose	Hydrolysis + Fermentation	0,36-0,66	€/L	(Hall & Taylor, 2006) / IEA
Bioethanol (near term)	Lignocellulose	Hydrolysis + Fermentation	0,35	€/L	(Kampman, Boer & Croezen, 2005)
Biomethanol	Lignocellulose	Gasification + Methanol synthesis	0,52	€/L	(DENA, 2006)
Bio-oil	Any type (<100€/ton)	Fast pyrolysis	0,06-0,25	€/L	(Thuijl, Roos & Beurskens, 2003)
DME	Lignocellulose	Gasification + Methanol synthesis	0,49	€/L	(Hall & Taylor, 2006) / IEA
DME	Wood	Gasification + Methanol synthesis + Catalytic Dehydration	0,27	€/L	(Thuijl, Roos & Beurskens, 2003)
ETBE	Sugar beet	Bioethanol conversion to ETBE	0,48	€/L	(Kampman, Boer & Croezen, 2005)
ETBE	Lignocellulose	Bioethanol conversion to ETBE	0,29-0,35	€/L	(Kampman, Boer & Croezen, 2005)

FT diesel	Lignocellulose	Gasification + FT synthesis	0,71	€/L	(Hall & Taylor, 2006) / IEA
FT diesel (long term)	Woody biomass	Gasification + FT synthesis	0,4	€/L	(Kampman, Boer & Croezen, 2005)
FT diesel (near term)	Woody biomass	Gasification + FT synthesis	0,76	€/L	(Kampman, Boer & Croezen, 2005)
Green diesel	Vegetable oil	Hydrogenation + Isomerisation	26-34	€/ton	(Kalnes, Marker, & Shonnard, 2007)
HTU diesel	Wet biomass	HTU	0,16-0,24	€/L	(Thuijl, Roos & Beurskens, 2003)
HTU diesel (long term)	Wet biomass	HTU	0,25	€/L	(Kampman, Boer & Croezen, 2005)
HTU diesel (near term)	Wet biomass	HTU	0,58	€/L	(Kampman, Boer & Croezen, 2005)
Methanol (long term)	Wood	Gasification + Methanol synthesis	0,1	€/L	(Thuijl, Roos & Beurskens, 2003)
Methanol (near term)	Wood	Gasification + Methanol synthesis	0,14-0,20	€/L	(Thuijl, Roos & Beurskens, 2003)
Hydrocarbons	Microalgae	Harvesting	0,48	€/L	(Schenk, et al., 2008)

Appendix 4 Development trends data

technology	products	development stage	challenges
FTS of biomass-derived syn-gas	liquid alkanes	large scale pilot plant	controlling selectivity during FTS process, Tar removal/ conversion from syn-gas
fermentation of biomass-derived syn-gas	ethanol	laboratory scale	development of enzyme catalysts
fast pyrolysis	bio-oils	commercial	bio-oils are unstable
liquefaction	bio-oils	pilot plant	bio-oils are unstable
hydrotreating of bio-oils	mixture of aromatics, alkanes	laboratory scale	bio-oils are unstable at high temperatures producing coke, requires expensive H ₂
zeolite upgrading (catalytic cracking) of bio-oils	mixture of aromatics, alkanes	laboratory scale	large amounts of coke produced, quality of final product low
fermentation of corn starch or sugarcane	ethanol	commercial	requires large amounts of energy for distillation
ethanol via fermentation of cellulosic biomass	ethanol	large scale pilot plant	conversion of cellulosic biomass to sugars, fermentation of C ₅ sugars, long residence times
hydrogenation of furfural (hemicellulose-derived)	methyl-tetrahydrofurfural	commercial for chemicals	not currently economical for fuels, need more efficient catalysts
aqueous-phase processing of sugar-derived feedstocks	straight chain alkanes (C ₁ –C ₁₆)	laboratory scale	need to test with real biomass feedstocks, need more efficient catalysts, multiple steps
esterification of levulinic acid	levulinic esters	laboratory scale	requires low-cost levulinic acid feedstock
hydrotreating of lignin	alkyl benzenes, paraffins	laboratory scale	conversion of solid lignin residue into a liquid; requires expensive H ₂
catalytic cracking of lignin	aromatics, coke	laboratory scale	large amounts of coke are produced
catalytic cracking of sugars	aromatics, coke	laboratory scale	large amounts of coke are produced
transesterification of vegetable oils	alkyl esters (bio-diesel)	commercial	high-cost of vegetable oils; need to replace mineral base catalysts.
hydrotreating of vegetable oils	alkanes (<i>n</i> -C ₁₂ –C ₁₈)	pilot plant	requires expensive H ₂
catalytic cracking of vegetable oils	aromatics, olefins, paraffins	laboratory scale	large amounts of coke are produced; multiple products produced

Figure 45. State of some biofuels technologies and challenges to overcome (Huber, 2006)

Fuel	Source	Benefits	Maturity
Grain/Sugar Ethanol	Corn, sorghum, and sugarcane	<ul style="list-style-type: none"> • Produces a high-octane fuel for gasoline blends • Made from a widely available renewable resource 	Commercially proven fuel technology
Biodiesel	Vegetable oils, fats, and greases	<ul style="list-style-type: none"> • Reduces emissions • Increases diesel fuel lubricity 	Commercially proven fuel technology
Green Diesel and Gasoline	Oils and fats, blended with crude oil	<ul style="list-style-type: none"> • Offer a superior feedstock for refineries • Are low-sulfur fuels 	Commercial trials under way in Europe and Brazil for fuel
Cellulosic Ethanol	Grasses, wood chips, and agricultural residues	<ul style="list-style-type: none"> • Produces a high-octane fuel for gasoline blends • Is the only viable scenario to replace 30% of U.S. petroleum use 	DOE program is focused on commercial demonstration by 2012
Butanol	Corn, sorghum, wheat, and sugarcane	<ul style="list-style-type: none"> • Offers a low-volatility, high energy-density, water-tolerant alternate fuel 	BP and DuPont plan to introduce butanol fuel in 2007
Pyrolysis Liquids	Any lignocellulosic biomass	<ul style="list-style-type: none"> • Offer refinery feedstocks, fuel oils, and a future source of aromatics or phenols 	Several commercial facilities produce energy and chemicals
Syngas Liquids	Various biomass as well as fossil fuel sources	<ul style="list-style-type: none"> • Can integrate biomass sources with fossil fuel sources • Produce high-quality diesel or gasoline 	Demonstrated on a large scale with fossil feedstocks, commercial biomass projects under consideration
Diesel/Jet Fuel From Algae	Microalgae grown in aquaculture systems	<ul style="list-style-type: none"> • Offer a high yield per acre and an aquaculture source of biofuels • Could be employed for CO₂ capture and reuse 	Demonstrated at pilot scale in 1990s
Hydrocarbons From Biomass	Biomass carbohydrates	<ul style="list-style-type: none"> • Could generate synthetic gasoline, diesel fuel, and other petroleum products 	Laboratory-scale research in academic laboratories

Most Mature

Least Mature

Figure 46. Study by NREL indicating the maturity of many technologies as well as their major benefits (Ashworth, 2006)

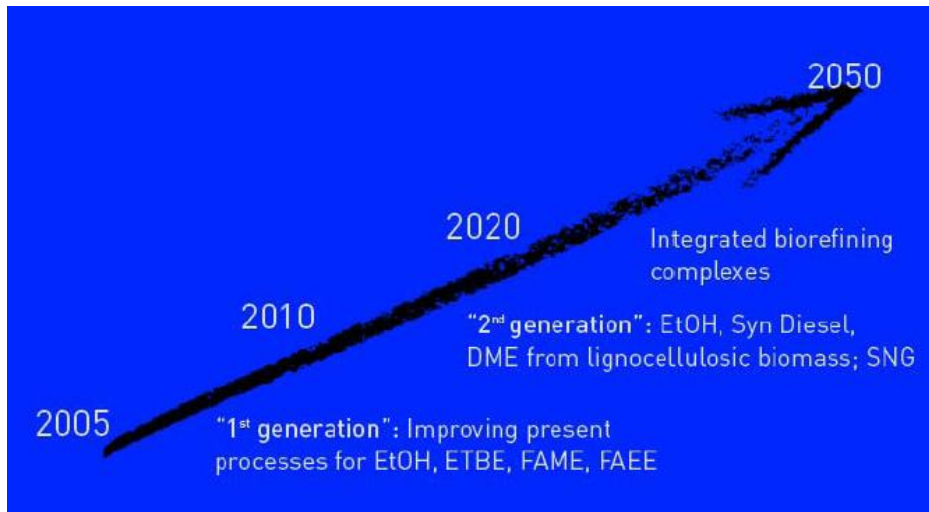


Figure 47. Prospect for European future in biofuels (Rutz & Janssen, 2007)

Development of biofuels

	"Traditional"	New generation
2010	Bio-diesel blends + pure Bio-ethanol blends + pure	FT from natural gas
2020	Bio-diesel blends Bio-ethanol blends	FT from woody biomass Ethanol from woody biomass Others such as SNG, DME, HTU
	Biodiesel and bioethanol fading out	FT from woody biomass Ethanol from woody biomass Hydrogen from woody biomass ?
		Integrated bio-refinery ?

Figure 48. Biofuels trends by Ecofys Academy (Harmsen, 2008)

Appendix 5 Bibliometric data

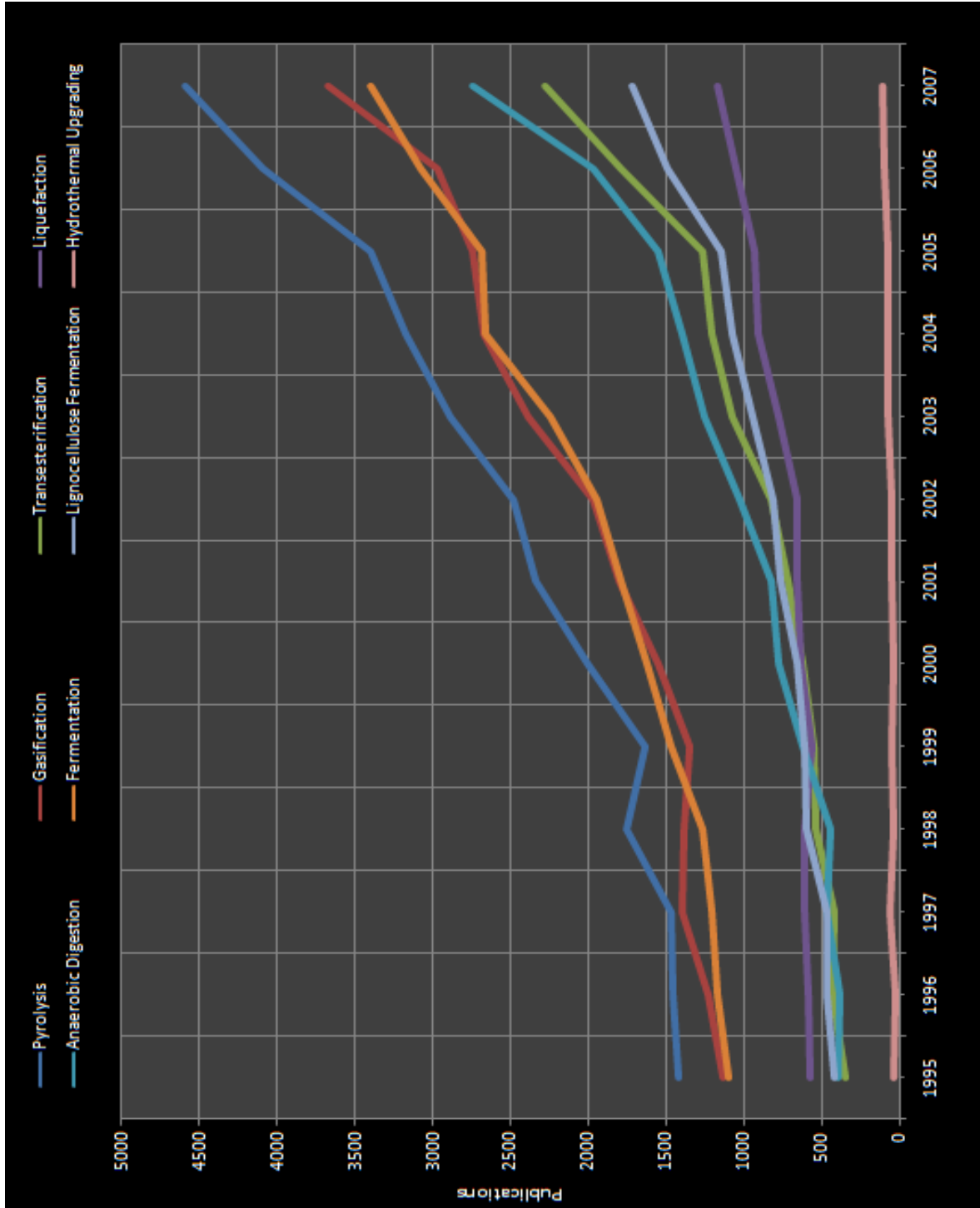


Figure 49. Annual number of publications on each technology research since 1995 (data obtained using Google Scholar)

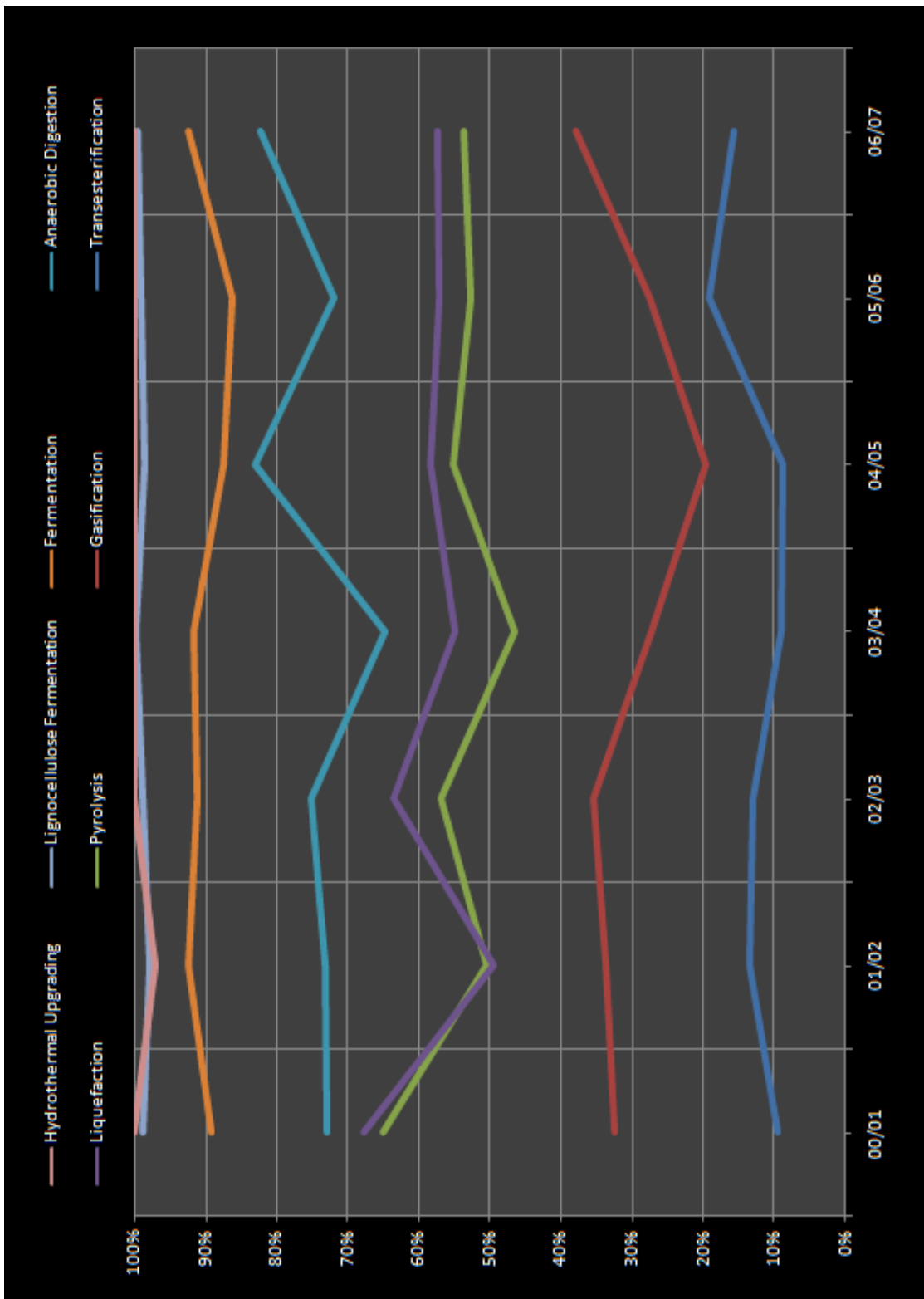


Figure 50. Acceleration rate of the publications number on each technology research since 1995 (data obtained using Google Scholar)

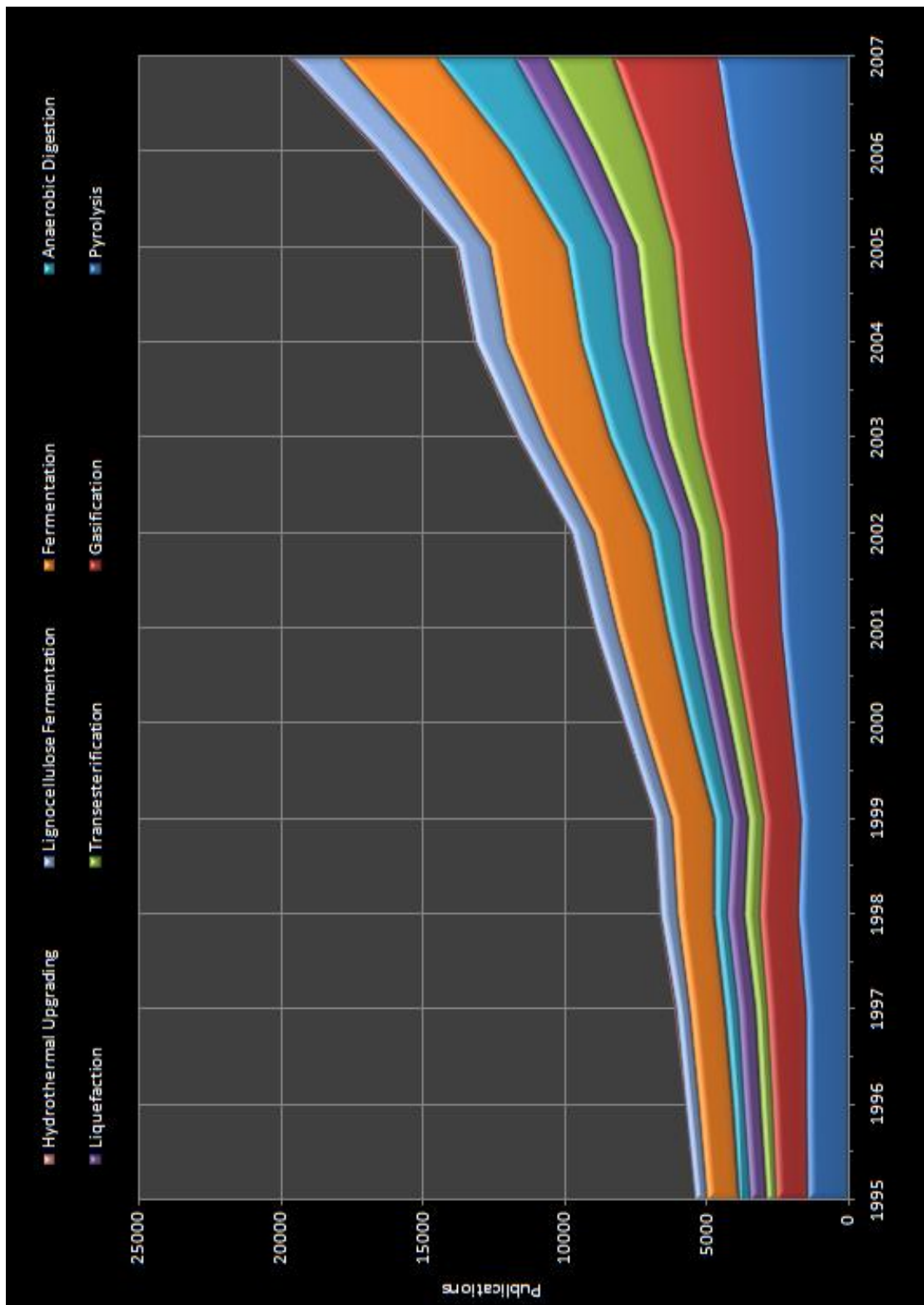


Figure 51. Cumulative annual number of publications on each technology research since 1995 (data obtained using Google Scholar)

Appendix 6 Algal biomass composition data

Table 4. Chemical characterization of algal biomass families (Heilbron, 1941)

Microalgae	Common characteristic	Core constitution	Cell wall constitution	Habitat
Chlorophyceae	Green algae	Usually starch	Mainly cellulose	Fresh water with marked terrestrial tendency; few marine
Xanthophyceae	Yellow-green algae	Usually oil or leucosin	Rich in pectin compounds and silica	Mainly freshwater
Chrysophyceae	Golden algae	Fats and leucosin	Pectin, cellulose, sometimes silica	Mostly freshwater, particularly plankton in lakes
Bacillariophyceae	Diatoms	Fats and volution, never starch	Pectin substances, impregnated with silica	Freshwater and marine
Cryptophyceae	With ejectisomes	Starch or starch-like compound	Mostly naked protoplast	Mostly freshwater; few marine
Dinophyceae	Main class of dinoflagellates	Starch and oil	Elaborated cellulose plates	Mostly marine
Raphidophyceae	Chloromonads	Oil		Freshwater only
Euglenineae		Paramylon (related to starch) or fats	Naked protoplast (no cell wall)	Almost all freshwater
Phaeophyceae	Brown algae	Stored in dissolved state like sugar-storing Higher Plants	Inner of cellulose, outer of pectin compound	Almost exclusively marine and generally colder waters
Rhodophyceae	Red algae	Insoluble floridean starch; some contain a galactoside of glycerol as well	Cellulose and pectin compounds	Mostly marine; few species in freshwater
Cynobacteria	Blue-green algae	Sugars and glycogen	Mainly cellulose; pectin outer; Mucilage coat	Mainly freshwater