Bio-syngas to gasoline and olefins via DME – A comprehensive techno-economic assessment

Abstract

The conversion of low-grade lignocellulosic biomass such as residual wood or straw to synthetic fuels and chemicals is currently being developed within the bioliq® concept (at the Karlsruhe Institute of Technology – KIT, Germany). The aim of this study is to model and assess three different synthesis process concepts with DME (dimethyl ether) as a platform chemical. The process concepts are designed and assessed using existing technologies, as well as the previous studies for pyrolysis and gasification sections. The respective considered products in the selected concepts are synthetic gasoline, ethylene and propylene. Using biomass for these applications can reduce fossil CO₂ emissions by replacing non-renewable carbon sources. The techno-economic assessment concludes that total energy efficiency ranges between 37.5% and 41.1% for the production of gasoline and olefins, respectively. The resulting specific production cost in the gasoline concept is 72% higher than the current market price. In the olefins concept the difference to the current market prices of ethylene and propylene is reduced to 40%. The specific production costs in the gasoline and ethylene concept are 59% higher than current market prices. The possibility to sequestrate CO₂ within the considered concepts at costs of 39 €/t allow additional revenues from sequestrated CO₂. In order to meet current market prices, the implications of sequestrated CO₂, mineral oil tax reduction and the combination of both kinds of subsidies are evaluated in this study.

Keywords: Techno-economic assessment; Thermochemical biorefinery; Process design and simulation; Dimethyl ether (DME); Gasoline; Olefins

1. Introduction

The European Union enforces the use of biomass derived transportation fuels by setting a share of 10% biofuels for 2020 [1]. Synthetic gasoline produced from biomass is one of the most promising alternative fuels since it can be used in regular internal combustion engines without modifications. Furthermore biomass can reduce fossil CO₂ emissions by replacing non-renewable carbon sources in other applications, such as in the chemical industry. The biobased production of olefins is a promising way to produce plastics from biomass. The integrated production of multiple products from biomass is currently discussed for future-expected thermochemical biorefineries using dimethyl ether (DME) as platform chemical, as for example using the DME (hydro)carbonylation route for the production of ethanol, methyl acetate DME and hydrogen from syngas (synthesis gas) [2]. In this study we assess the production of olefins and gasoline separately, i.e. two different concepts, and also the co-production (multiproduction) of gasoline and ethylene.

Nomenclature

BTL: biomass-to-liquid CC: combined cycle DME: dimethyl ether HHV: high heating value

IGCC: integrated gasification combined cycle

LPG: liquefied petroleum gas

MOGD: Mobil olefins-to-gasoline and distillate process

MTG: methanol-to-gasoline
MTO: methanol-to-olefins
PSA: pressure swing adsorption

RKS-BM: Redlich-Kwong-Soave with Boston-Mathias modifications

SRK: Soave-Redlich-Kwong WWT: waste water treatment

The biolig® concept, which is currently being developed at the Karlsruhe Institute of Technology (KIT) [3], allows the conversion of low-grade lignocellulosic biomass such as residual wood or straw to synthetic fuels and other chemicals, as illustrated in Figure 1. The biolig[®] concept offers a two-stage approach to cope with the comparably low energy density of biomass. The first stage consists of multiple decentralized pyrolysis plants to liquefy the biomass collected from a radius of about 30 km around each pyrolysis plant. The slurry, which is a mixture of pyrolysis oil and char, offers a tenfold increased volumetric energy density and allows economical transportation over long distances to the centralized large scale gasification and synthesis plant [4]. The capacity of the gasification and synthesis plant should be as large as possible in order to profit from economies of scale and produce more efficiently and cost-effectively [5]. Pressurized entrained flow gasification is the technology currently best suited to process capacities of up to 1 GW of bio-slurry (thermal input) [4]. After cleaning and conditioning, the syngas can be used to synthesize fuels or chemicals by different pathways. The system boundaries of this study are limited to those of the synthesis section as shown in Figure 1. For the synthesis section, three concepts for gasoline, olefins and gasoline & ethylene production are designed. In earlier studies the authors assessed the pyrolysis step [6] as well as the production of syngas by entrained flow gasification [7]. The techno-economic assessment of the considered concepts is based on the results of the previous conversion steps of the bioliq® concept (pyrolysis and gasification).

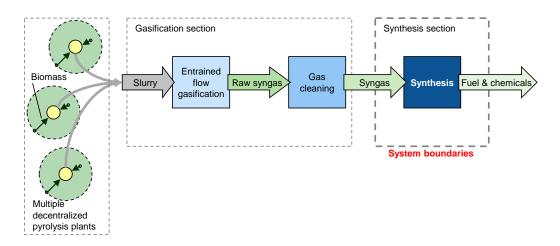


Figure 1. Overview of the bioliq® concept and system boundaries of this study.

The production of gasoline from coal or natural gas (through syngas) was a subject of interest during the 1980's due to the oil crisis. A few commercial plants were operated using the MTG (methanol-to-gasoline) technology or combining the MTO (methanol-to-olefins) and MOGD (Mobil olefins-to-gasoline and distillate process) technologies for gasoline production. These plants were shut down after the recovery of crude oil prices [8]. Currently, such processing is regaining attention but using biomass instead of coal as feedstock. A previous techno-economic assessment focusing on the conversion of coal into gasoline was carried out by Bridgwater et al. [9]. The study assessed the MTG and MTO-MOGD technologies, among others, technically and economically. Current studies are limited to the production of synthetic gasoline using biomass as feedstock [10-13]. Furthermore, the co-feeding of coal and natural gas in a plant producing synthetic gasoline has also been assessed [14]. The production of olefins from coal or natural gas (through syngas) was of less interest than the production of gasoline. The MTO technology, jointly developed with MTG, was implemented by Norsk Hydro in Norway using natural gas as feedstock [15]. However, there are currently several plants operating in China using coal as feedstock [16, 17]. The production of olefins from coal or natural gas instead of crude oil is a possible solution for the expected propylene gap, since (opposite to the refining of crude oil) the proportion of ethylene to propylene can be adjusted [18]. A previous study assessed the MTO process using lignocellulosic biomass as feedstock and demonstrated that the process could be cost-competitive at high crude oil price [18].

This study investigates the realization of the bioliq[®] concept converting clean and conditioned biomass-derived syngas in three different synthesis process alternatives (see Figure 1). The selected technologies in this assessment are currently available and have been demonstrated using coal or natural gas as feedstock. The whole plant is designed and assessed with realistic data and avoiding the assumption of future or expected (uncertain) developments. The biomass-derived syngas feed in all three concepts is first converted into DME. Different process conditions and catalysts in the DME conversion reactor lead to the production of gasoline or olefins. In the gasoline concept the main product is gasoline. Lighter hydrocarbons are used as

fuel gas to generate electricity. Ethylene and propylene are the main products in the olefins concept. In this concept fuel gas is also used for electricity generation. The gasoline & ethylene concept combines the production of gasoline and olefins by using the olefins to gasoline process. Propylene and higher olefins are converted into gasoline whereas ethylene is recovered as product. For the considered concepts, two syngas feedstock options each are assessed which leads to six different cases.

Within the techno-economic assessment in this study the considered concepts are compared in terms of energetic efficiency and production costs. First the technology involved in converting syngas into gasoline and olefins and the respective process designs are presented. Following the methodology for the process modeling and techno-economic assessment is provided. The economic assumptions are based on a near future realization of the bioliq[®] concept in Germany. The results of mass and energy balances, investment estimation and production costs are outlined for each concept. The production costs of the respective products are compared to current market prices. Implications of CO₂ sequestration and mineral oil tax reductions on minimum product selling prices are discussed. Finally a sensitivity analysis for the economic results is conducted and conclusions of this study are drawn.

2. Process description and design

This section provides the definition of the input to the system boundaries in this study (synthesis section, see Figure 1), a summary of the technology involved in the main conversion steps and the process design for the considered synthesis concepts.

2.1. Syngas feed

The input for all considered concepts is the cleaned and conditioned syngas, with a molar H_2 :CO ratio of 1, from the gasification section [7]. The syngas is fed to the synthesis plant at a temperature of 35 °C and with pressures of 35 or 75 bar for the 40 and 80 bar cases, respectively. The 40 and 80 bar cases represent two alternatives in the current technological development of the bioliq[®] process in the pilot plant in Karlsruhe and are therefore assessed in this study.

2.2. DME synthesis

Commercial processes for the production of DME from syngas are proven technology by companies like Haldor Topsoe A/S, Toyo Engineering Ltd., Air Liquide, S.A. or JFE Holding Inc. This study considers a single step reactor where methanol synthesis and in situ dehydration take place (commercial JFE's process [19]), as shown in the following equation:

$$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2 \tag{1}$$

The advantage of the single step DME reactor is that syngas with an H₂:CO ratio of 1 – which is close to the natural composition of biomass-derived syngas – yields higher CO conversions than methanol synthesis. Data for process conditions of the DME synthesis reactor are shown in Table 1.

Table 1. Process conditions of the DME synthesis reactor (adapted from [20-22]).

	()	- [-]/
Temperature (°C)		250
Pressure (bar)		35
CO conversion		0.85
Product distribution (% mass fracti	ons)	
	DME	49.3
	MeOH	1.4
	CO_2	48.8
	H ₂ O	0.5

2.3. Gasoline and olefins synthesis and upgrading

Gasoline production from methanol was developed in the 1980s in response to the oil crisis. Several facilities were constructed but most of them were shut down when oil prices made the process unprofitable [23]. Such facilities could also use DME or mixtures of DME and methanol as feedstock [24]. Kinetics for the methanol and/or DME to gasoline conversion is described in [25]. Chang and Silvestri [25] found the dehydration of methanol to be the only difference between methanol and DME conversion without effect on the hydrocarbon distribution. The DME to hydrocarbon conversion is a complex reaction pattern of methylation, oligomerization, hydrocarbon formation and cracking using zeolites as catalyst [26]. The data for the process conditions of DME to gasoline reactors are shown in Table 2. The conversion of DME into gasoline results in about 22% light gases, 66% hydrocarbons in the light gasoline range and 12% on mass basis in the heavy gasoline range. The most prominent compound of the heavy gasoline fraction is durene (1,2,4,5-tetramethyl-benzene) which needs to be further processed in order to meet current gasoline specifications. The durene is isomerized to compounds with lower melting points in a fixed bed reactor in presence of hydrogen at 32 bar and 220 °C [10]. The upgraded heavy gasoline is blended with the light gasoline fraction to give total production of commercial grade gasoline.

The olefins production from methanol was developed along with gasoline production from methanol [23]. The reactor designs used in the gasoline production can also be used in the production of olefins. Differences can be found in catalysts and process conditions. In general, catalysts for the production of olefins are characterized by smaller pore sizes compared to production of gasoline [26]. Lower partial pressures of DME and higher reaction temperatures lead to a shift in the product distribution to lighter hydrocarbons [25]. Table 2 shows the main products ethylene and propylene make up about 84% on mass basis of total hydrocarbons produced.

A part of the olefins produced by the considered process can be converted into gasoline using similar catalysts as described by [30]. Olefins are fed to a fixed bed reactor operating at 30 bar and 340 °C and completely converted. This gasoline is advantageous compared to the above mentioned process in terms of gasoline quality, e.g. there is no significant durene content [25,26,30].

Table 2. Process conditions of DME to gasoline and DME to olefins reactors (are adapted from [10,11,18,25,27-29]).

		Gasoline	Olefins
Temperature (°C)		380	450
Pressure (bar)		33	4
DME conversion		1.0	1.0
Inert compounds (% v/v)	CO_2 , CO , H_2 , H_2O	66.5	39.1
Hydrocarbon distribution (% mass)			
	Ethylene	0.8	45.1
	Propylene	0.4	38.7
	Other light gases	18.2	7.9
	Butenes	2.5	8.3
	Light gasoline	66.3	-
	Heavy gasoline	11.8	-

2.4. Process design

Following, an overview of the process configurations selected for the techno-economic assessment of the synthesis section is provided taking the layouts from related references [8-11] as basis for the design. For each of the three considered concepts, the process from biomass-derived syngas to the respective final products is described.

The process flowchart of the gasoline concept is illustrated in Figure 2. In the 80 bar case the syngas is first expanded to meet the DME synthesis pressure of 35 bar. This brings an additional possibility in the 80 bar cases to generate electricity which is not available in the 40 bar case. Downstream of this point the 40 and 80 bar cases are identical. The syngas is led through the DME synthesis reactor and the whole outlet stream is heated up to 300 °C and sent to the gasoline synthesis reactor. The DME and gasoline synthesis reactors allow the generation of steam which is used for heat and power integration in the gasification and synthesis plant. The product stream of the gasoline synthesis reactor is degasified to remove unconverted syngas and CO₂ which make up about molar 60%. The required amount of hydrogen for the downstream isomerization reactor is recovered from the distillate stream in a pressure swing adsorption (PSA) unit. The bottom stream is led to a decanter where water is removed from liquid hydrocarbons. The recovered water is led to waste water treatment (WWT). Raw gasoline is split up into light and heavy fractions. Dissolved gases are removed from the light gasoline in a fractionation column. The heavy gasoline enters an isomerization reactor where durene is converted to a compound with lower melting point. The outlet stream is cooled

and led to a gas-liquid-separator where hydrogen and light hydrocarbons are recovered. This and other fuel gas streams, shown in Figure 2, are fed to the gas turbine of the combined cycle to generate power. The waste heat of the gas turbine is used for high pressure steam generation. This is used in the steam turbine together with the steam generated by the gasoline synthesis reactor. The steam generated in the DME synthesis reactor serves for the thermal integration of the fractionation columns.

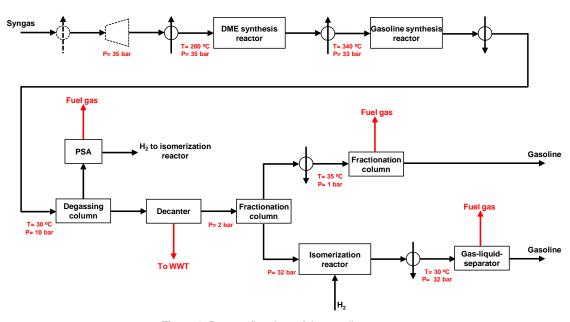


Figure 2. Process flowchart of the gasoline concept.

Figure 3 illustrates the process flowchart of the olefins concept. In analogues lines with the gasoline concept the expansion of the syngas in the 80 bar case is the only difference between the 40 and 80 bar cases. The outlet stream of the DME synthesis reactor is cooled before entering the first cryogenic fractionation column where unconverted syngas is removed. The separation of unconverted syngas from the product stream downstream of the olefins synthesis reactor would be less efficient. In order to meet the reaction conditions for the olefins synthesis, the pressure is decreased to 4 bar. The heat released in the olefins synthesis is used to reheat the reactor feed and to generate high pressure steam. Before entering the product recovery, the outlet stream of the gasoline synthesis reactor has to be recompressed and dewatered as well as CO₂ has to be removed. A Rectisol® unit operating at 39 bar [31,32] is used to separate the CO2. The recovered CO2 stream meets the requirements for subsequent transportation and sequestration. The downstream dewatering unit removes traces of water before entering the product recovery. First C₂₋ and C₃₊ hydrocarbons are split in a cryogenic fractionation column. The distillate stream is led to a cryogenic de-methanizer column where methane and traces of unconverted syngas are recovered. The bottom stream is fed to a cryogenic de-ethanizer column where ethylene and LPG (liquefied petroleum gas) are separated. The C₃₊ hydrocarbons enter a de-butanizer column where LPG, i.e. butenes, is recovered as bottom. The distillate goes into a de-propanizer column where propylene and LPG are separated.

Finally, total LPG contains about 60% butenes, 20% propane and 20% ethane on mass basis. The LPG product stream lowers the amount of fuel gas available for the gas turbine in the combined cycle. The waste heat of the gas turbine is also used for high pressure steam generation. This is used in the steam turbine together with the steam from the olefins synthesis reactor. The steam generated in the DME synthesis reactor is used for the thermal integration of the fractionation columns.

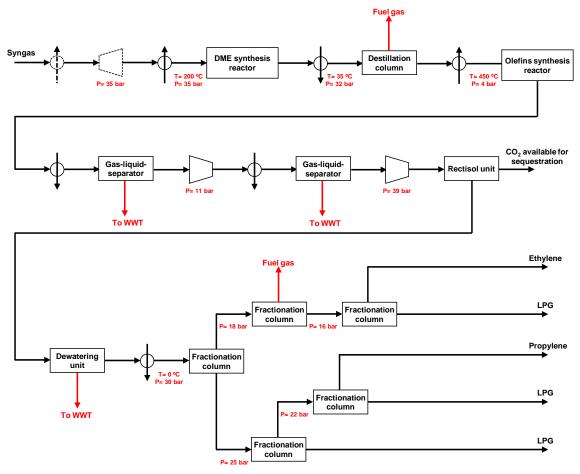


Figure 3. Process flowchart of the olefins concept.

As illustrated in Figure 4 the gasoline & ethylene concept is identical to the olefins concept except for the product recovery. In the gasoline & ethylene concept there is no LPG production and ethane recovered in the de-ethanizer column is used as fuel gas. The C_{3+} hydrocarbons are fed to the gasoline reactor. Since there is no water in the outlet stream of the gasoline reactor, only light hydrocarbon have to be removed. Because there is no LPG production the electricity generation in the combined cycle is increased compared to olefins concept.

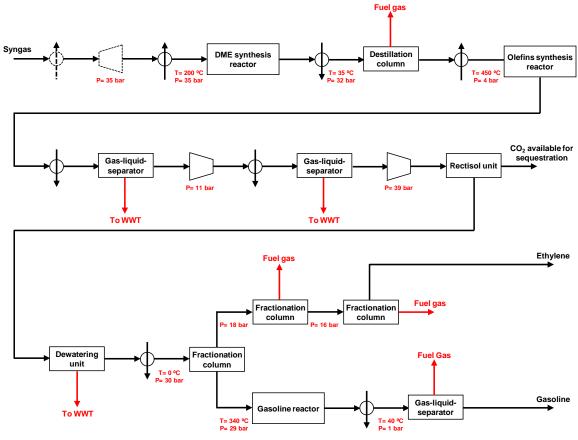


Figure 4. Process flowchart of the gasoline & ethylene concept.

3. Methodology

In order to conduct the techno-economic assessment for the considered gasoline and olefins production concepts, the mass and energy flows within the system boundaries are analyzed first. For this purpose, the process simulation software Aspen Plus is used. The mass and energy flow balancing builds up the foundation for the economic assessment. Fixed capital investment estimated for the respective equipment is derived using the determined capacities. Investment dependent costs together with personnel and other operating costs, as well as revenues from by-products, lead to specific production costs for the considered products in each concept. Finally, the robustness of the applied methodology is discussed.

3.1. Process modeling

Below, the most important criteria and assumptions used to simulate the considered concepts are outlined. The thermodynamic method used to model the high pressure processing is Soave–Redlich–Kwong (SRK). The low pressure processing is modeled using Redlich–Kwong–Soave with Boston-Mathias modifications (RKS–BM). These thermodynamic methods give accurate results in modeling hydrocarbon and light gases [33]. According to the experimental results of [21,22], an equilibrium reactor is used for the DME synthesis. The specific product yields of the DME to gasoline, DME to olefins and olefins to gasoline reactors are calculated in a spreadsheet using the distribution of hydrocarbons, according to Table 2,

and fixing the remaining products to meet the atom balance. The isomerization of heavy gasoline is carried out in a RStoic reactor (stoichiometric reactor) where durene is assumed to be converted to 1,2,3,4-tetramethyl-benzene [10]. The modeling of synthesis reactors is summarized in Table 3.

Table 3. Reactor types used in Aspen Plus.

Process step	Туре
DME synthesis reactor	REquil (equilibrium reactor)
Gasoline synthesis reactor	RYield (yield reactor)
Isomerization reactor	RStoic (stoichiometric reactor)
Olefins synthesis reactor	RYield (yield reactor)
Gasoline reactor	RYield (yield reactor)

Rigorous fractionation columns, i.e. RadFrac, are used to give accurate results in the product recovery. Column design and modeling in terms of molar split fractions, optimization of utility consumption and thermal integration of columns was performed according to [34]. Thermal integration of the considered concepts is carried out by using a minimum temperature difference of 20 °C for steam heating and generation as well as for water cooling. A minimum temperature difference of 40 °C is imposed for gas-to-gas heat transfer. An inventory of heat demand and supply is used to find the optimum thermal integration of each concept [2;35].

The process turbine and compressors as well as the gas and steam turbines in the combined cycle were modeled by assuming common isentropic and mechanical efficiencies [36] and according to Smith [34]. The gas turbine of the combined cycle is fed with high-pressure fuel gas streams, except in the case of gasoline concept, where the off-gas stream from the PSA unit needs to be compressed before entering the gas turbine. However, the overall efficiency of the combined cycle in this concept is still of 56%.

3.2. Economic assumptions

The economic assessment aims to determine gasoline and olefins production costs for six cases, i.e. three considered concepts and two syngas feed options each. To achieve this goal, the fixed capital investment for the considered concepts as described in the previous chapter is estimated. All equipment components are designed according to the mass and energy flows.

Investment data for the main equipment components are summarized in Table 4. Investment data for equipment components not listed in Table 4, e.g. heat exchanger and distillation columns, are calculated according to [38,39]. The investment data are converted into €, using the yearly average exchange rate of the respective year, and updated to the year 2010 [40]. To account for price developments of equipment components, the price index from Kölbel/Schulze [41] is used.

Based on the investment data for the main equipment components listed in Table 4, the total capital investment can be estimated using ratio factors for direct and indirect capital investment according to [38], as presented in Equation 2. Table 5 summarizes the assumed ratio factors for the control system, piping and further direct capital investments as well as the ratio factor for indirect capital investments, such as engineering or legal expenses. The ratio factors are selected according to process conditions, design complexity and required materials in this study. The applied ratio factor method implies uncertainties of ±30% [38].

The parameters presented in Table 6 used to calculate the investment dependent costs have also been used in the calculations for the pyrolysis plants and the gasification section. Further information about the methodology can be found in [6;7]. The syngas feedstock costs and prices, respectively, are adapted from previous studies by the authors and are based on biomass feedstock costs of 71 € per dry ton. The biomass feedstock costs include the transportation to the pyrolysis plants. If there is a net electricity surplus the revenue for electricity is supposed to be the same as the price in case of a net electricity demand. The stated price for hydrocarbon catalyst is applied for DME to gasoline, DME to olefins and olefins to gasoline catalysts.

Table 4. Summary of investment data for main equipment components (installed).

Description	Base Description Unit		М€	Scaling	Reference
Description	scale	Onit	2010	Factor ^a	Reference
DME synthesis reactor	2.7	kmol of total feed/s	8.2	0.65	[37]
Gasoline synthesis reactor	1,347	kmol of DME/h	2.8	0.65	[11]
Olefins synthesis reactor	1,347	kmol of DME/h	6.0	0.72	adapted from [15]
Isomerization reactor	4,673	kg of heavy gasoline/h	1.8	0.70	[37]
Gasoline reactor	1,137	kmol of carbon feed/h	1.6	0.65	[11]
Hydrogen recovery unit	0.6	kmol of purge gas/s	4.0	0.74	[37]
Hydrogen compressor	0.7	MW_e	0.3	0.67	[37]
Rectisol® unit	44,141	Nm ³ of total feed/h	10.4	0.65	assumed
Cryogenic system	6.8	MW_{th}	6.0	0.70	[38]
Gas turbine	86.7	MW_e	12.1	0.75	[37]
Steam generator	317.0	MW_{th}	18.4	1.00	[37]
Steam cycle	141.0	MW_e	19.3	0.67	[37]

^a The scaling factor (n) is used to scale the investment of the equipment from the base scale to the design scale,

$$\frac{\mathit{Investment}}{\mathit{Investment}_{\mathit{base}}} = \left(\frac{\mathit{Design scale}}{\mathit{Base scale}}\right)^{n}.$$

Table 5. Ratio factors for direct and indirect capital investment (adapted from [38]).

Direct investments	%
Investment for installed equipment	100
Instrumentation and control	24
Piping	46
Electrical systems	8
Buildings	12
Yard improvements	7
Service facilities	48
Total direct investment	245
Indirect investments	%
Engineering and supervision	22
Construction expenses	28
Legal expenses	3
Contractor's fee	15
Contingency	30
Total indirect investment	98
Fixed Capital Investment	343

Fixed capital investment = $I_{IE} \cdot [1 + \sum_{i=1}^{n} f_i]$

(2)

 I_{IE} Investment for installed main equipment components

 f_i Ratio factor for direct/indirect capital investment i = 1...n

Table 6. Summary of economic assumptions.

Parameters for investment dependent costs					
Capacity factor	%	80			
Expected lifetime	Years	20			
Depreciation (no scrap value)	linear	-			
Interest rate	%	7.0			
Working capital	% of fixed capital investment	5.0			
Maintenance costs (average)	% of fixed capital investment	3.0 - 3.6			
Insurance & taxes	% of fixed capital investment	2.0			
F	rices for consumables				
Syngas 40 bar (adapted from [7])	€/Nm ³	0.243			
Syngas 80 bar (adapted from [7]) ^a	€/Nm ³	0.238			
Electricity [42]	€/MWh	99.3			
Cooling water [11]	€/m ³	0.26			
Waste water treatment [7]	€ /m³	0.32			
DME catalyst costs [10]	€ /kg	22			
Hydrocarbon catalyst [10]	€ /kg	113			
Market prices of products (without taxes)					
Gasoline (2011 average, [43])	€/L	0.651			
Ethylene (2011 average, [44])	€/t	1,140			
Propylene (2011 average, [44])	€/t	1,120			
LPG (assumed by authors)	€/kg	0.980			

^a The syngas with 80 bar pressure can be produced at lower costs because the efficiency of the entrained flow gasifier is higher at 80 bar (see [7] for details).

4. Results

The following section summarizes the resulting mass and energy balances as well as fixed capital and production costs estimations. The results for the six cases are listed. They comprise two kinds of syngas input for the gasoline, olefins and gasoline & ethylene production concepts. The different pressure levels of syngas are due to the respective operating pressure in the entrained flow gasifier. However, there is only one pressure level in the considered hydrocarbon synthesis options. The most prominent consequence is an additional electricity generation possibility in the 80 bar cases.

4.1. Mass and energy balances

Table 7 illustrates the mass and energy balances for the gasoline, olefins and gasoline & ethylene production from biomass-derived syngas. In all considered processes the syngas input is identical in terms of mass flow and HHV (higher heating value) content. In the gasoline production concept the difference between the 40 and 80 bar cases is the generation of about 5 MW additional electricity which is the consequence of the higher pressure in the syngas input. This is also applicable for the olefins and gasoline & ethylene production concept, since the DME synthesis is always operated at same conditions. Compared to the gasoline concept, the total hydrocarbon production in the olefins and the gasoline & ethylene concepts is 23% and 16% higher. On the opposite side, the gasoline concept leads to the highest electricity generation by converting a higher amount of fuel gas in the combined cycle. The electricity generation in the olefins and gasoline & ethylene concept is about 70% and 57% lower. However, the net electricity generation stated in Table 7 is only referring to the generation and consumption within the synthesis section (system boundaries of this study). The global electricity balance, also shown in Table 7, includes the pyrolysis plants and gasification section.

$$Energy \ efficiency = \frac{products \ (MW_{th})}{biomass \ (MW_{th}) + \frac{net \ electricity}{\eta_e}(MW_{th})} \tag{3}$$

In order to make a fair comparison of all concepts the total energy efficiency from biomass to final products is also shown. The additional upstream electricity consumption in the pyrolysis plants as well as the gasification and gas cleaning accounts for 68 and 66 MW in the 40 and 80 bar case, respectively. This leads to an additional electricity input in the olefins and gasoline & ethylene production. The additional electricity input is converted to an HHV equivalent by assuming conversion efficiency (biomass to electricity) of 39% (typical for an IGCC plant using biomass). The total energy efficiency calculated according to Eq. (3) ranges between 37.5% and 41.1% corresponding to the gasoline and the olefins concepts. The gasoline & ethylene concept lies in between the other concepts, but is closer to the gasoline concept. In terms of energy efficiency the olefins concept prevail over the other concepts. Increased hydrocarbon production leads to higher efficiencies. Furthermore the specific HHV on mass basis of olefins compared to the average of gasoline is about 5% higher. Regarding the whole biolig[®] plant the energy losses of the gasoline concept are described in Figure 5, where the energy content of biomass is expressed on HHV basis. Major efficiency losses occur before the synthesis section, i.e. the pyrolysis of biomass reduces the energy content by about 15% and the gasification has an efficiency of about 78%.

Table 7. Mass and energy balances for the considered process concepts.

	••						
	Gasoline		Ole	Olefins		& Ethylene	
	40 bar	80 bar	40 bar	80 bar	40 bar	80 bar	
	Input to	o system bo	oundaries				
Syngas in t/h (MW HHV)	144	144	144	144	144	144	
	(760)	(760)	(760)	(760)	(760)	(760)	
	Output fr	om system	boundaries	;			
Gasoline in t/h (MW HHV)	30.0	30.0			18.2	18.2	
	(394)	(394)	-	-	(239)	(239)	
Ethylene in t/h (MW HHV)			16.6	16.6	16.6	16.6	
	-	-	(230)	(230)	(230)	(230)	
Propylene in t/h (MW HHV)			14.3	14.3			
	-	-	(199)	(199)	-	-	
LPG in t/h (MW HHV)			6.0	6.0			
	-	-	(84)	(84)	-	-	
Electricity generation in MW net	117	123	34	39	49	54	
(gross)	(123)	(128)	(55)	(60)	(70)	(75)	
Electricity balance in MW ^a	-49	-57	34	27	19	12	
Energy efficiency in % (HHV basis)							
From syngas to products ^b	67.2	68.0	72.0	72.6	68.1	68.8	
From biomass to products ^c	37.5	38.2	40.5	41.1	38.1	38.7	

^a Refers to the global electricity balance of the whole bioliq[®] concept, including the pyrolysis plants and the gasification and synthesis plant. A positive value indicates that electricity is imported.

$$Energy \ efficiency = \frac{products \ (MW_{th}) + output \ electricity \ (MW_e)}{syngas \ (MW_{th}) + \frac{input \ electricity}{\eta_e} (MW_{th})}.$$

^b The energy efficiency from syngas to products refers to the efficiency of the synthesis plant assessed in this study.

 $^{^{\}circ}$ The energy efficiency from biomass to final products is calculated using Eq. (3).

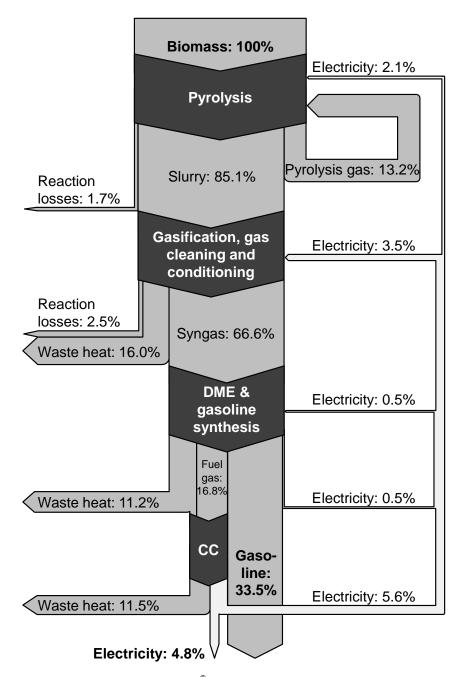


Figure 5. The Sankey diagram of the whole bioliq® plant for the gasoline concept (80 bar). CC: combined cycle.

4.2. Economic evaluation

Figure 6 shows the fixed capital investment corresponding to the system boundaries of this study. Comparing the 40 and 80 bar cases within the different production concepts, the increase in fixed capital investment is mainly caused by the additional process turbine. The gasoline concept requires the lowest investment. The synthesis and product recovery make up about half of the fixed capital investment, the other half belongs to the power island. The investment for synthesis and product recovery in the olefins concept is twice as high, but the power island accounts for only half compared to the gasoline concept. This is mostly due to the more capital intensive product recovery and additional equipment in between the synthesis steps as shown in Figure 3. The investment for the gasoline & ethylene concept is close to the olefins concept, since the process design is the same, but the propylene recovery which is replaced by the olefins to hydrocarbon synthesis. The realization of the whole bioliq[®] concept including entrained flow gasification, gas conditioning and cleaning as well as about 10 decentralized pyrolysis plants with 100 MW_{th} capacity to meet the slurry consumption of the gasification and synthesis plant is adding 930 and 890 M€ for the 40 and 80 bar cases, respectively, to the above mentioned fixed capital investment.

The specific production costs for the considered concepts are presented in Figure 7. The production costs are indicated in € per kg of hydrocarbon to help the comparison of respective products. Due to the system boundaries in this study the syngas costs include the total upstream operating costs. For this reason there are electricity revenues in all cases regardless of total net electricity generation or consumption in each case (see also Table 7). The syngas costs are by far the largest contributor to the production costs. The final specific production costs of hydrocarbons from biomass in the gasoline concept are the lowest. The sum of the production costs (excluding revenues) in the gasoline concept is close to the olefins concept, but the revenues for excess electricity lead to a difference of 0.08 € per kg of hydrocarbons. In the olefins case the hydrocarbon products are ethylene and propylene. The lower electricity revenues in the olefins concept are only partly compensated by LPG revenues. In the gasoline & ethylene concept the specific syngas costs are lower, but this is due to the higher hydrocarbon production. This is also applicable to the other operating cost components in analogue lines.

For the calculation of specific production costs in Table 8 the prices of by-products, i.e. electricity and LPG, are fixed (see Table 6). For the gasoline concept the specific production costs are 77% and 72% higher than the current market price (shown in their common units: per litter and per GJ). For the olefins concept the difference to the current market prices of ethylene and propylene is reduced to 44% and 40%. The specific production costs in the gasoline & ethylene concept are 63% and 59% higher than current market prices. For the calculation in the concepts with two main products, we assume that the relation between specific production costs remains the same as in the current market prices. Considering mineral oil taxes in Germany the

selling price for gasoline is not about 0.651 €/L, but 1.306 €/L ([43]). To be competitive to fossil gasoline, tax reductions for biomass-derived gasoline could be a solution. This is discussed in the next section.

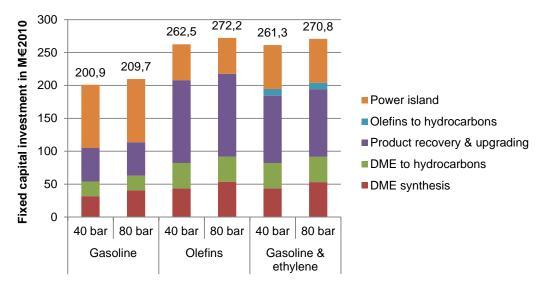


Figure 6. Fixed capital investment for the considered process concepts.

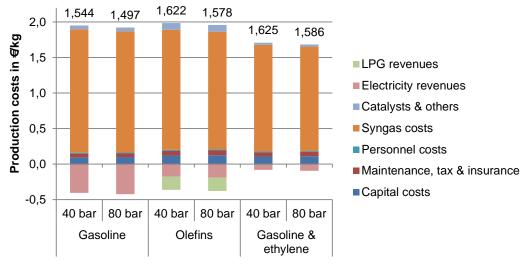


Figure 7. Specific production costs on mass basis.

Table 8. Specific production costs for main products in the considered concepts.

	Gasoline		Olefins		Gasoline & Ethylene	
	40 bar	80 bar	40 bar	80 bar	40 bar	80 bar
Gasoline in €/L	1.154	1.119	-	-	1.059	1.034
Gasoline in €/GJ	41.25	40.64	-	-	37.32	36.80
Ethylene in €/t	-	-	1,635	1,591	1,853	1,809
Propylene in €/t	-	-	1,607	1,563	-	-

5. Implications of CO₂ sequestration and mineral oil tax reductions

As described in the economic results the specific production costs for gasoline and olefins produced from biomass are currently not competitive. In the before mentioned process designs there is CO_2 available for sequestration. Since all the CO_2 available for sequestration comes from biomass which is neutral in climate change regulations, the effect of the CO_2 sequestration can be translated into avoided emissions. These avoided emissions have not been regulated yet. For the following assessment, the authors assume that there is the possibility to sell these avoided emissions via CO_2 certificates.

In the following analyses only the more promising 80 bar cases presented in Chapter 4.2 are evaluated. The CO_2 emissions due to the pyrolysis, gasification and synthesis steps are similar for all concepts, as presented in Table 9. The higher emissions in the gasoline and gasoline & ethylene concepts result from lower hydrocarbon production. There is CO_2 available for sequestration in the gas cleaning section of all concepts. In the olefins and gasoline & ethylene concepts there is additional CO_2 available in the synthesis section (the system boundaries of the study).

In order to meet technical specifications for transport and sequestration, the CO_2 removed from the process has only to be compressed (see 2.3). The authors assume that a pressure of 100 bar is sufficient for transportation and subsequent sequestration [45]. Additional capital and operating costs are caused by the compressors which amount to $20 \in per t$ of CO_2 . Including transportation and sequestration, the total CO_2 mitigation costs amount to $39 \in per t$ of CO_2 . This leads to the conclusion that CO_2 would be sequestrated for prices of CO_2 certificate higher than $39 \in t$.

Table 9. Summary of CO₂ emissions, sequestration and mitigation costs.

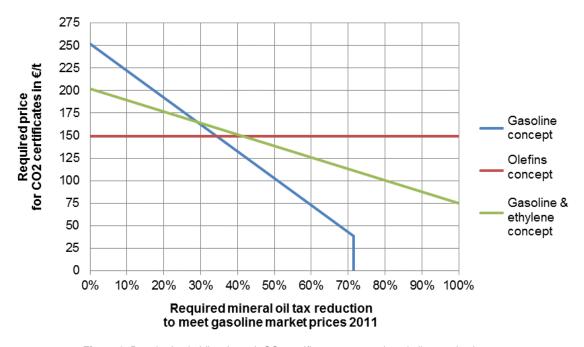
		Gasoline	Olefins	Gasoline & Ethylene
CO ₂ emissions from biomass conversion	TOTAL	319.2	295.7	302.7
	Pyrolysis ^a	89.9	89.9	89.9
	Gasification ^a	101.5	101.5	101.5
	Synthesis	127.8	104.3	111.3
CO ₂ available for sequestration in t/h	TOTAL	88.0	125.3	125.3
	Gasification ^a	88.0	88.0	88.0
	Synthesis	0	37.4	37.4
CO₂ transportation costs in €/t	[45]			4
CO₂ sequestration costs in €/t	[45]			14
Total CO₂ mitigation costs in €/t				39

^a Outside of system boundaries in this study.

Figure 8 compares the possibilities of subsidies for the considered products from industry via CO_2 certificates and from public sector via mineral oil tax reductions. Using CO_2 certificates to make the considered products profitable leads to 150 $\mbox{\ensuremath{\notin}} t$ in the olefins concept, 202 $\mbox{\ensuremath{\notin}} t$ in the gasoline & ethylene concept and up to 252 $\mbox{\ensuremath{\notin}} t$ in the gasoline concept. The IEA (International Energy Agency) considers prices of up to 200 $\mbox{\ensuremath{\notin}} t$ for CO_2 certificates in Europe in 2040 ([45]). In the gasoline concept there is no longer an effect of CO_2 certificates prices as soon as it drops below 39 $\mbox{\ensuremath{\notin}} t$.

Since the prices for CO₂ certificates are far from current market prices, mineral oil tax reductions are another option to strengthen the competitiveness in the medium term. Of course, the tax reductions would only have an impact on gasoline. In order to meet the current market price for gasoline a mineral oil tax reduction of 71% would be required. Even a tax reduction of 100% would not be enough to make the gasoline & ethylene concept competitive. There is no impact of tax reduction in the olefins concept.

Evaluating the ranking of the considered concepts, three areas can be distinguished in Figure 8. In case of mineral oil tax reductions of less than 30% the olefins concept would be most promising. For mineral oil tax reductions of more than 40% the gasoline concept would be first to become competitive. If mineral oil tax reductions range between 30% and 40%, the difference between the respective concepts is not significant.



 $\textbf{Figure 8}. \ \ \text{Required subsidies through CO$_2$ certificates versus mineral oil tax reductions.}$

6. Discussion and sensitivity analysis

The before mentioned results of this study show that the production of gasoline and olefins from biomass is not competitive at current market prices. However, this is not a result of the technology involved, but of the assumed biomass feedstock costs. To demonstrate the competitiveness of the technologies scenarios with 90% coal and 10% biomass-derived slurry on energy basis as input in the gasification are analyzed. The coal price used in the calculation is 107 €/t which corresponds to the yearly average of 2011 in Germany ([42]). The specific production costs of gasoline are 0.663 and 0,691 €/L in the gasoline and gasoline & ethylene concepts, respectively. The specific production costs of ethylene are 996 and 1,208 €/t in the olefins and gasoline & ethylene concepts, respectively. All the calculated prices in this scenario are very close to the current market prices, so the technology is competitive to conventional refinery processes. These results are in agreement with the recent interest of some companies in the construction of new MTO and MTG plants using coal [16,17]. Except for the coal fed, the calculation of these specific production costs is conducted with the same assumptions as for the results presented in Table 8. In comparison to related studies for the production of gasoline from biomass through syngas [10,11,13], the process layout and efficiencies are similar (except the efficiency for [13] which is larger). The production costs of this study are twice the values of references [11,13] and slightly above to those of reference [9]. The main reason for the discrepancies with previous assessment relies on the different assumptions of each study. Whereas in these related studies, assumptions of expected improvements have been made for the gasification [13], conversion technologies [11,13] or feedstock cost ([11] uses 56 US\$ per dry tonne versus 71 € per dry tonne of this study); this study is focused on the realization of the bioliq® concept using technical data from the plant in Karlsruhe and only currently commercial technologies with realistic assumptions. Hence, this study achieves the highest production costs of all the studies from the literature of synthetic gasoline production. In case of olefins production there is only one reference and the results are similar to those presented here [18].

The reduction of mineral oil taxes and the selling of CO₂ credits are potential subsidies to support the process' profitability. Looking for a medium term scenario, where the expected improvement in gasification and syngas conversion technologies are not available, the sought of extra revenues must be accomplished. The reduction of mineral oil taxes is a known option, already in use in some countries to enhance the production and consumption of biofuels. The possibility of CO₂ storage and sequestration in the assessed plants (pre-combustion) has a better economy than in regular power plants (post-combustion) and, due to the neutral origin of the carbon, can be sold as CO₂ credits (emissions trading).

An important contribution of this study is the combination of two different but related BTL (biomass-to-liquid) processes for the production of gasoline and ethylene from biomass-derived syngas. This design of a thermochemical biorefinery, i.e. a thermochemical processing plant with multiproduction of gasoline and ethylene is firstly proposed. Benefits of thermochemical

biorefineries are still on discussion, but they bring a better position for market fluctuations, since the production is diverted into different sectors (energy and petrochemicals).

The effect of the biomass feedstock price on the specific production cost of gasoline is illustrated in Figure 9. As mentioned before the biomass feedstock costs also include the transportation costs to the pyrolysis plants. A doubling of biomass feedstock costs results in a 38% increase in the specific production cost of gasoline. Figure 10 shows the effect on the olefins concept. Since there are two main products in this case, the weighted average of ethylene and propylene specific production costs is calculated. A doubling of biomass feedstock costs in this concept leads to a 35% increase in the specific production cost of olefins.

As mention in the methodology, the fixed capital investment method has an accuracy of ±30%. To evaluate the sensitivity of specific production costs to the total fixed capital investment, the conservative deviation of +30% is calculated for the gasoline and olefins concepts. In order to make a fair analysis the fixed capital investment of the pyrolysis and gasification steps are also included. In the gasoline concept an increase of 30% in total fixed capital investment results in a 16.5% higher specific production cost. In the olefins concept this increase leads to 16.1% higher specific production cost. The high sensitivity to changes in the fixed capital investment emphasizes the importance of profiting from economies of scale as intended by the bioliq[®] concept.

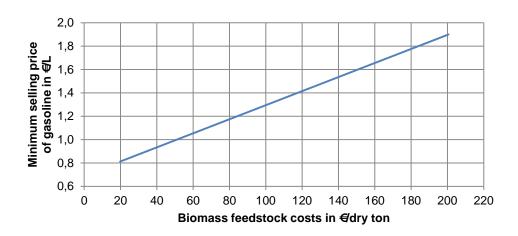


Figure 9. Sensitivity of gasoline specific production cost to biomass feedstock cost.

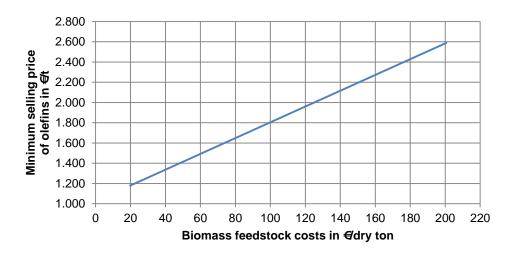


Figure 10. Sensitivity of average ethylene and propylene specific production cost to biomass feedstock cost.

7. Conclusions

A comparative techno-economic assessment for the realization of the bioliq[®] concept for the production of gasoline, olefins and gasoline & ethylene is performed. The three considered concepts use DME as a platform chemical. Previously to this study, the pyrolysis and gasification steps were designed and assessed with realistic data (from the bioliq[®] plant in Karlsruhe). These assessments build up the basis for the assessment of the synthesis section. The three different synthesis concepts described in this study are modeled using commercial technologies for the conversion of DME using coal and natural gas. The combination of two different, but related, BTL processes for the production of gasoline and olefins is proposed as an example of the design of a thermochemical biorefinery. This concept (gasoline & ethylene) achieves the multiproduction without penalization of economics or efficiency with respect to the case of single gasoline and olefins production.

The total energy efficiency ranges between 37.5% and 41.1% corresponding to the gasoline and the olefins concepts. Resulting specific production costs in the gasoline concept are 77% and 72% higher than the current market price for the 40 and 80 bar cases, respectively. For the olefins concept the difference to the current market prices of ethylene and propylene is reduced to 44% and 40%. The specific production costs in the gasoline & ethylene concept are 63% and 59% higher than current market prices. This is not a result of the technologies involved, but of the biomass feedstock costs. The possibility to sequestrate CO₂ within the considered concepts at costs of about 39 €/t allow additional revenues from CO₂ sequestration. This possibility is analyzed for the more promising 80 bar cases. In order to make the considered products profitable, CO₂ certificate prices of 150 €/t in the olefins concept, 202 €/t in the gasoline & ethylene concept and up to 252 €/t in the gasoline concept would be required. The reduction of mineral oil tax is also considered. To meet the current market price for gasoline with only tax reduction, a reduction of 71% would be necessary in the gasoline concept. The combination of both kinds of subsidies is also evaluated in this study.

The results of the assessment show that the production costs of the considered products are far from current market prices, which prevents potential investors from using biomass. Process development in order to achieve higher efficiencies or simpler process designs with lower capital requirements are one way towards competitiveness. Nevertheless, the results also point out that the public sector might enhance the competitiveness by implementing subsidies and/or regulation on CO₂ emissions.

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