

Thermochemical biorefinery based on dimethyl ether as intermediate: Technoeconomic assessment

Abstract

Thermochemical biorefinery based on dimethyl ether (DME) as an intermediate is studied. DME is converted into methyl acetate, which can either be hydrogenated to ethanol or sold as a co-product. Considering this option together with a variety of technologies for syngas upgrading, 12 different process concepts are analyzed. The considered products are ethanol, methyl acetate, H₂, DME and electricity. The assessment of each alternative includes biomass pretreatment, gasification, syngas clean-up and conditioning, DME synthesis and conversion, product separation, and heat and power integration. A plant size of 500 MW_{th} processing poplar chips is taken as a basis. The resulting energy efficiency to products ranges from 34.9% to 50.2%. The largest internal rate of return (28.74%) corresponds to a concept which produces methyl acetate, DME and electricity (exported to grid). A sensitivity analysis with respect to total plant investment (TPI), total operation costs (TOC) and market price of products was carried out. The overall conclusion is that, despite its greater complexity, this kind of thermochemical biorefinery is more profitable than thermochemical bioprocesses oriented to a single product.

Keywords: Thermochemical biorefinery; Technoeconomic assessment; Biomass; Methyl acetate; Ethanol; DME

1. Introduction

The thermochemical conversion of biomass to syngas (gasification) allows catalytic synthesis of chemicals and fuels. A large number of studies have been published on direct synthesis of liquids and gaseous biofuels such as ethanol, Fisher-Tropsch diesel, gasoline and SNG (substitute natural gas). However, studies on the co-production of biochemicals and biofuels via indirect synthesis routes are scarce. Ethanol production from lignocellulosic biomass via dimethyl ether (DME) hydrocarbonylation was assessed by the authors [1], revealing that this indirect route is more cost-competitive than state of the art routes of bioethanol production [1]. This paper explores the potential of such a biorefinery by polygenerating high-value chemical products (methyl acetate and H₂), liquid transportation fuels (ethanol and DME) and electricity. The high-value products enhance profitability, the fuel is helpful to meet national energy needs and the power production reduces costs and avoids greenhouse-gas emissions.

Nomenclature

ASU: Air Separation Unit
ATR: Autothermal Reformer
BTL/G: Biomass To Liquids/Gases
CR: Cryogenic Cooling
CW: Cooling water
DCFA: Discounted Cash Flow Analysis
DME: Dimethyl ether
EFG: Entrained Flow Gasifier
HHV: High Heating Value
HP: High Pressure
HRSG: Heat Recovery Steam Generation
iCFBG: Indirectly-heated atmospheric Circulating Fluidized Bed Gasifier
IRR: Internal rate of return
LP: Low Pressure
MA: Methyl acetate
MP: Medium Pressure
NRTL: Non-Random Two Liquid
PSA: Pressure Swing Adsorption
RKS—BM: Redlich—Kwong—Soave with Boston—Mathias alpha function
SNG: Substitute Natural Gas
SR: Steam Reformer
TOC: Total Operation Costs
TPI: Total Plant Investment
TR: Tar cracker/Methane Reformer

Twelve process concepts of the thermochemical biorefinery are assessed and compared. All alternatives use DME as an intermediate. In the first stage, DME is converted into methyl acetate by heterogeneous catalytic carbonylation. The catalyst for this reaction has been recently developed at laboratory scale [2-4]. In the second stage, the methyl acetate is either converted into ethanol and methanol or directly sold as a high-value product*. The methanol is converted into DME, increasing the overall ethanol yield. In addition to ethanol and methyl acetate production, the biorefinery concepts considered here include the production of H₂, DME and electricity. The DME can be converted in the plant or sold as a product, the relative proportion of each fraction being determined by the design of the DME conversion section. The production of the other two products, i.e. H₂ and electricity, is selected on the basis of the technology chosen for syngas clean-up and conditioning.

All process concepts have been technically assessed using data both from research literature and technology owners. Economic evaluation is based on data taken from vendors,

* Methyl acetate is currently available as a byproduct of acetic acid production or it can be produced by the esterification of methanol and acetic acid (reactive distillation) [5]. The main uses of methyl acetate are as a solvent (substitute for acetone) [6] and the production of acetic anhydride [7], one of the most important organic intermediates [8].

manufacturers and published BTL/G (biomass to liquids/gases) studies. A sensitivity analysis based on total plant investment (TPI), total operating costs (TOC) and market price of products is also made.

2. Conceptual design of alternatives

Figure 1 shows the scheme of reaction of the species involved in the process (syngas generation excluded). Two main alternatives are shown, according to the DME conversion path: DME carbonylation and DME hydrocarbonylation. The reaction steps involved in Figure 1 are: syngas (CO , H_2) to methanol, dehydration of methanol to DME, carbonylation of DME to methyl acetate, and hydrogenation of methyl acetate to methanol and ethanol.

Production of DME from syngas can be carried out either by direct conversion of syngas (one step) or by methanol synthesis and subsequent dehydration to DME. In this work, the one step process has been selected due to its higher CO per-pass conversion and the availability of technical data.

The catalytic carbonylation of DME over zeolites, e.g. H-Mordenite, has been recently demonstrated at lab scale [9-11]. Methanol can also be carbonylated to methyl acetate, but deactivation of the catalyst by the generated water occurs. The hydrogenation of acetates is a well-known process for which different catalysts have been developed [2-4, 12-14]. In this work, data from various recent developments have been considered: (i) for the hydrocarbonylation cases a combination of a carbonylation (H-Mordenite) and a hydrogenation (Cu-ZnO) catalyst is used. The performance of these catalysts has been successfully tested in a dual fixed bed reactor fed with syngas and DME [2-4], whereas the technical considerations are taken from [1]; (ii) experimental data and reactor conditions for DME carbonylation, are taken from [4]. These studies have shown that a large excess of CO in the reactor is necessary for both hydrocarbonylation and carbonylation of DME. Therefore, in the present work, these ratios are used: CO/DME molar ratio of 10 for hydrocarbonylation [3] and of 47.1 for carbonylation [4].

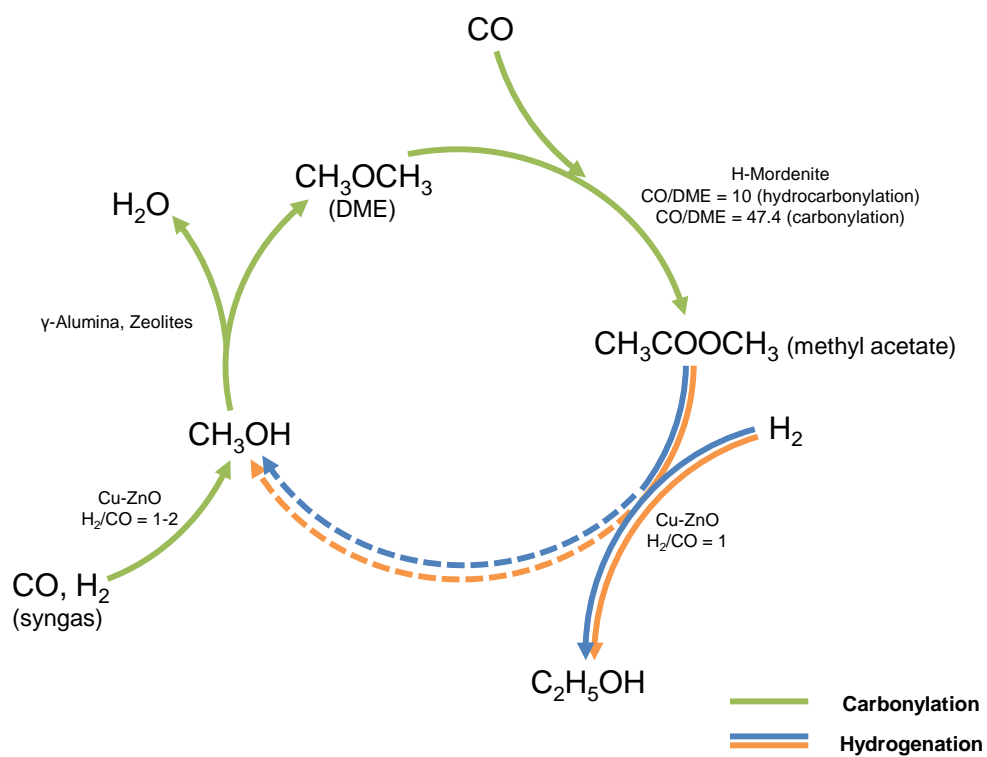


Figure 1. Chemical scheme illustrating the routes from syngas to different products through DME. The two main DME conversion routes are shown: carbonylation and hydrocarbonylation (carbonylation followed by hydrogenation). Dashed lines refer to the possibility of "extra" methanol dehydration to DME through methanol synthesis.

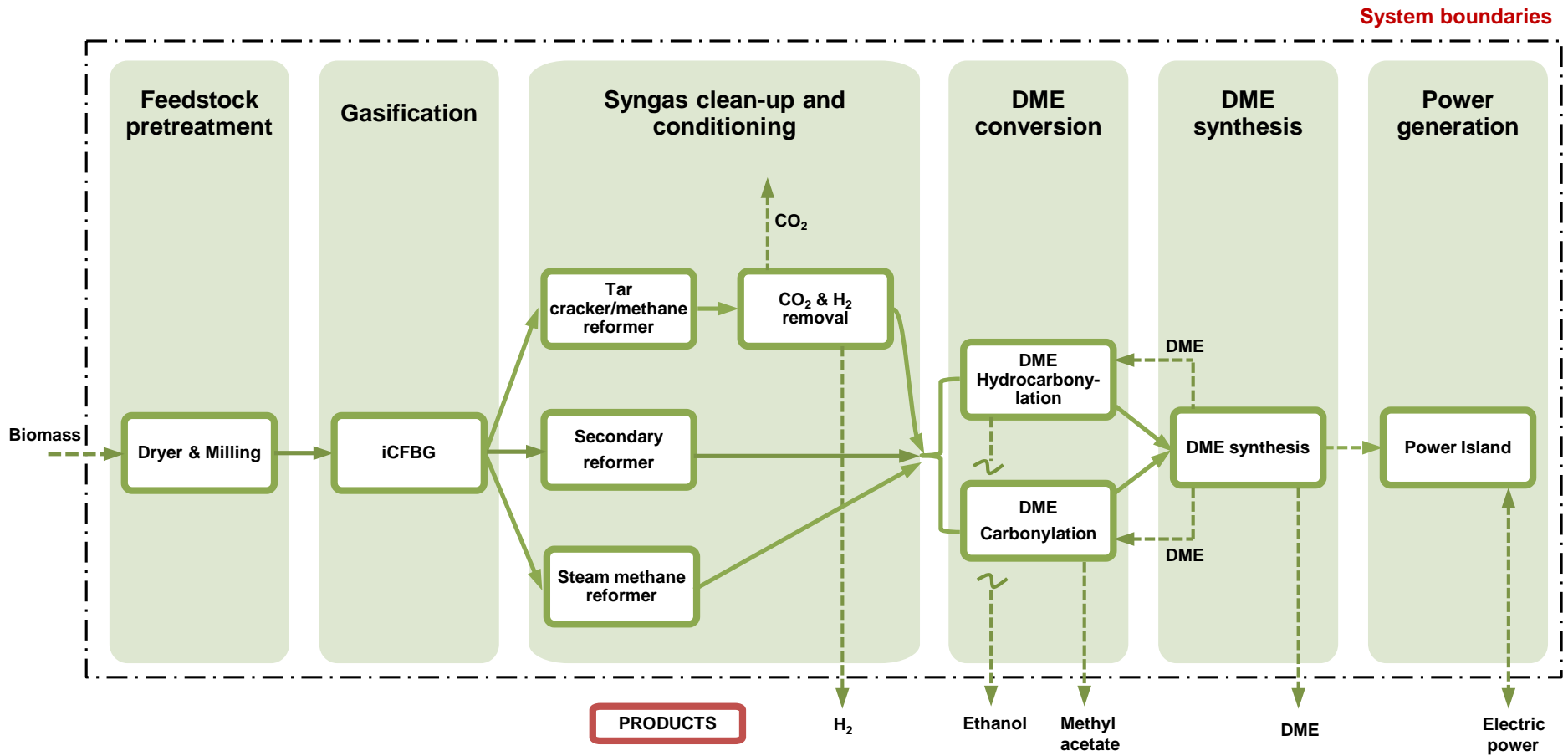


Figure 2. Layout of the process concept alternatives analyzed in the present work.

Figure 2 shows the layout for considered process concepts. Pretreated biomass is converted into syngas in an indirectly-heated circulating fluidized bed gasifier (iCFBG) operated at atmospheric pressure. The raw syngas is cleaned-up and conditioned. Three alternatives have been considered for these processes: a steam reformer (SR), a secondary autothermal reformer (*secondary-ATR*) and a tar cracker/methane reformer (TR). In the case of TR, the syngas has to be conditioned by CO₂ and H₂ removal (recovery) systems in order to meet the requirements of the synthesis catalytic reactor. The recovered H₂ can be sold or sent to a gas turbine for power generation, leading to two different alternatives.

After the upgrading stage, the syngas is sent to the DME conversion section. This is the main difference of the present approach compared to conventional processes, where syngas would be sent to a DME synthesis section. The ground relies on the large excess of CO required in the DME conversion reactor. In the case of the DME synthesis section prior to the conversion section, the total amount of CO would not be enough to achieve the required CO/DME ratio without recirculation of the unconverted syngas in the conversion loop. Hence, if the fresh syngas is used in the DME conversion section, it is found that there is still enough for DME synthesis, it avoids syngas recirculation to produce methyl acetate/ethanol (no recycle-compressor is necessary) and reduces some operating costs, e.g. the syngas should not be compressed to the DME synthesis pressure (50 bar), but only to the DME conversion pressure (10-30 bar).

For the DME conversion section, two alternatives are considered, i.e. DME carbonylation and hydrocarbonylation leading to the 6 different process alternatives up to this point (by considering the upstream options for the syngas upgrading). For the DME hydrocarbonylation concepts, we have considered two additional alternatives: extra production of DME or higher power generation, leading to a total of 12 process concepts. In the case of the DME hydrocarbonylation concepts, the produced methanol is always removed by condensation and sent for dehydration in the DME synthesis reactor.

For all process concepts, the gas from the DME synthesis reactor and other gas streams produced in the process are used to produce power and to satisfy the heat demand. Some alternatives produce an excess of electricity, i.e. more than that required for self-consumption, so there is a net power production, whereas other concepts need to import power.

To sum up, the products considered in the present work are:

- **Methyl acetate.** Produced within DME carbonylation concepts. The production is determined by the design of DME conversion section.
- **Ethanol.** Produced within DME hydrocarbonylation concepts. The production is determined by the design of DME conversion section.
- **H₂.** Produced only in TR concepts, where the H₂ in the syngas is in excess with respect to that required for DME hydrocarbonylation and DME synthesis.
- **DME.** It is considered as an alternative for DME hydrocarbonylation concepts and it is always produced in DME carbonylation concepts. The DME product achieves commercial grade and can be directly sold in the market.
- **Electric power.** Produced in some process concepts as a result of process configuration selected for some alternatives.

3. Detailed design and description of alternatives

3.1. Basis for design

The system boundaries for the process concepts considered are shown in Figure 2. The design basis and inputs are shown in Tables 1 and 2. For all alternatives the biomass feedstock is poplar chips. Table 1 also includes the design basis used in literature studies for comparison. Detailed data is presented in the Supplementary Information.

Table 1. Design basis for the alternatives of this work together with others taken from the literature.

	This study	[1]	[15]	[16]
Feedstock	Poplar chips	Poplar chips	Poplar chips	Hybrid poplar
Plant size (dry tonnes/day)	2140	2140	2140	2000
Plant size (MW _{th} on HHV basis)	500	500	500	466
Gasifier	iCFBG	iCFBG	EFG	iCFBG
Energy self-sufficient criterion ^a	No	Yes	Yes	Yes
Electrical energy neutral criterion ^b	No	Yes	Yes	Yes
Feedstock price (USD ₂₀₁₀ /dry tonne)	66	66	66	51
Target	Polygeneration	Ethanol	Ethanol	Ethanol

HHV: high heating value; EFG: entrained flow gasifier.

^a The energy self-sufficient criterion means that the only energy input is biomass.

^b The electrical energy neutral criterion means that the required power is produced within the plant.

Table 2. Properties of biomass feedstock (poplar chips).

Component	% wt, dry basis
Carbon	50.90
Hydrogen	6.05
Oxygen	41.92
Nitrogen	0.17
Sulphur	0.04
Ash	0.92
Moisture	30% wt
HHV	20.18 MJ/kg

3.2. Process description

The thermochemical biorefinery concepts are compiled in Table 3, along with their assigned codes. Process alternatives for each one are also identified.

Table 3. Definition of the biorefinery process concepts.

	SR-01	SR-02	SR-03	ATR-01	ATR-02	ATR-03	TR-01	TR-02	TR-03	TR-04	TR-05	TR-06
Product												
Methyl acetate			✓			✓					✓	✓
Ethanol	✓	✓		✓	✓		✓	✓	✓	✓		
H ₂								✓		✓	✓	
DME		✓	✓		✓	✓			✓	✓	✓	✓
Electric power	✓	✓	✓	✓	✓	✓	✓	✓	✓	*	*	✓
Process alternatives												
Steam reformer (SR)	✓	✓	✓									
Secondary reformer (<i>secondary-ATR</i>)				✓	✓	✓						
Tar cracker/methane reformer (TR)							✓	✓	✓	✓	✓	✓
CO ₂ removal system							✓	✓	✓	✓	✓	✓
H ₂ separation unit							✓	✓	✓	✓	✓	✓
DME Carbonylation			✓			✓					✓	✓
DME Hydrocarbonylation	✓	✓		✓	✓		✓	✓	✓	✓		

The concepts marked with * require an external supply of electric power.

3.2.1. Feedstock pretreatment

Biomass feedstock with 30 wt% moisture is dried in a rotary dryer, where moisture is reduced to 12 wt% with combustion gases from the gasifier (iCFBG). The gas has been previously cooled from 800°C down to 450°C to produce high pressure (HP) steam in a heat recovery steam generator (HRSG). Dried poplar chips are sent to a hammer mill for particle reduction below 4 cm.

3.2.2. Gasification

For the synthesis of liquid fuels and other chemicals only a nitrogen-free syngas is suitable. Three gasification technologies can be considered: (a) EFG, (b) CFBG with O₂ and steam and (c) iCFBG using air and steam. The first two technologies are directly-heated oxygen-blown gasifiers, whereas the third operates with air and does not need an ASU (air separation unit) plant. EFG and iCFBG have been previously considered in prior studies aimed at ethanol production [15, 17]. An EFG was disregarded because processes based on this gasifier were found to be more expensive than those based on iCFBG for all alternatives analyzed [17]. The selected atmospheric iCFBG was modeled considering experimental data [18]. The performance data of the iCFBG is shown in Table 4.

Table 4. iCFBG operating parameters, exit gas composition and efficiency.

Gasifier Performance^{a, b}	
Pressure	1.5 bar
Temperature	900 °C
Steam (2 bar, 140°C)/dry	0.4 kg/kg
Biomass	
Heat loss in gasifier	1.53% HHV
Cold gas efficiency (%HHV)	77.07
Component	mole (%)
H ₂	14.55
CO	23.64
CO ₂	6.92
H ₂ O	43.43
CH ₄	8.43
NH ₃	0.18
Tars	0.15
C2+	2.70
H ₂ S	184 ppm

^a Dust, nitrogen and alkali compounds, and halogens are not included.

^b Case of tar recirculation to the combustor of the gasifier; when there is no tar recirculation to combustor, raw syngas flow and composition change according to iCFBG model.

3.2.3. Gas clean-up and conditioning

The raw syngas from the gasifier contains dust, tars, nitrogen and alkali compounds, and halogens which must be removed in order to prevent damage to equipment and the poisoning of catalysts. Two possibilities to remove the tars from the raw syngas are considered: (1) oil and water scrubbing (for SR and ATR concepts), and (2) TR along with water scrubbing. Removal of particles is carried out in both cases by high-temperature cyclones. Sulphur compounds (H_2S and COS) are removed by a liquid phase oxidation process (LO-CAT[®]) and bed filtration (ZnO). The syngas is then conditioned to meet the requirements of the downstream catalysts in the reaction loop: a H_2/CO ratio of 1, a low content of CO_2 (<10%v/v) and hydrocarbons (mainly methane) in the DME conversion section, and syngas dewatering. For tar and light hydrocarbon reforming some alternatives have been studied in previous BTL/G publications (SR, ATR and TR, used alone or in combination with removal systems for H_2 and CO_2) [15, 16, 19-28]. In this work, three alternatives for syngas reforming are considered: SR, secondary reformer (*secondary-ATR*) and TR. These processes have been modeled using technical data of natural gas reforming (for SR and *secondary-ATR*) and experimental data (for the TR) [29].

3.2.3.1. Steam Reforming (SR)

In these concepts the gas from the gasifier is de-dusted in a high efficiency cyclone and cooled down to 400°C in a HRSG. Then it is sent to an OLGA[™] system where tars are removed by oil-scrubbing [30]. Collected tars and waste solvent are recycled and burned in the riser (combustor) of the gasifier. Nitrogen compounds, alkalis and HCl are removed by water scrubbing. The cleaned syngas is compressed up to 17 bar and desulphurized in the LO-CAT[®] system where H_2S is oxidized to elemental sulphur [31, 32]. The concentration of H_2S is further reduced in a Co-Mo/ ZnO dual bed, where hydrogenation of olefins into paraffins also takes place. The desulphurized syngas enters the SR where methane and light paraffins are converted into syngas. The H_2/CO ratio is adjusted by setting the steam to hydrocarbon ratio, ensuring no carbon deposition over the catalyst. The reformed syngas is cooled, compressed and dehydrated in a molecular sieve, preventing the presence of water in either the DME hydrocarbonylation or in the DME carbonylation reaction section [1].

3.2.3.2. Autothermal Reforming (ATR)

The alternatives using ATR have the same cleaning system as those for SR. The *secondary-ATR* reformer is a mature technology for gas streams with a low hydrocarbon content [25]. Both steam and oxygen are fed to the secondary reformer, which operates at 32 bar. Due to the low consumption of oxygen in the secondary reformer, oxygen production in an ASU plant is not considered, but the oxygen is imported.

3.2.3.3. Tar Reforming (TR)

The raw syngas enters the TR free of particles. Design of this system is made on the basis of recent experimental data [29] obtained for a given catalyst and operating temperature (see Supplementary Information for more details). The outlet stream is cooled and the remaining impurities (dust, alkalis, residual ammonia, etc.) are removed by water scrubbing. Then, the cleaned syngas is compressed and desulphurized as in SR-concepts.

3.2.3.4. Removal of CO₂ and H₂

The CO₂ and H₂ removal (recovery) is not carried out in process alternatives with SR or secondary reformer, since both reforming technologies allow adjustment of the steam to hydrocarbon ratio. In TR cases, the steam to hydrocarbon ratio is determined by the gasifier; the CO₂ concentration in the syngas is high and the H₂/CO ratio is about 1, close to that required in the process. For example, in the TR-03 concept (production of ethanol, DME and electric power), the CO₂ concentration in the DME synthesis loop accumulates up to 52%v/v if CO₂ is not removed, resulting in the necessity of large equipment. The selected technology for CO₂ removing is an amine system, due to the low partial pressure of CO₂ in the gas. A PSA (pressure swing adsorption) system is selected for recovering the excess of H₂. This H₂ may be sold as a product or burned in gas turbine for power generation.

3.2.4. DME conversion section

As described above, there are two alternatives depending on whether DME hydrocarbonylation or DME carbonylation is applied. In all cases, the DME conversion section is designed as multi-stage reactors with DME shots. In the cases based on DME hydrocarbonylation, there are also inter coolers and gas-liquid separators, as shown in Figure 3. This configuration fits process requirements best because it enables high DME conversion in the reactor and does not require syngas recirculation to fulfill the high CO/DME ratio required, like in the case of using a single reactor. For the DME hydrocarbonylation concepts, the recovery of liquid products (ethanol and methanol) is necessary in order to avoid degradation of products in the next reactor stage. As shown in Figure 3, conditioned and dewatered syngas is fed to the first stage together with the corresponding amount of DME. In this work, a reactor with 5 stages has been selected for both DME carbonylation and hydrocarbonylation.

3.2.4.1. DME hydrocarbonylation

For the design of the DME hydrocarbonylation section, a CO/DME ratio of 10 was used on the basis of recent results [1]. Collected liquid products from the reactors (methanol, ethanol and small amounts of methyl acetate) are mixed and sent to the product separation section.

3.2.4.2. DME carbonylation

For the design of the DME carbonylation section, all concepts are designed and modeled using a CO/DME ratio of 47.1 in the presence of H₂. Methyl acetate and some ethyl acetate are recovered by cryogenic cooling and sent to the product separation section.

3.2.5. DME synthesis

The DME synthesis section is modeled using information of the JFE's process [33], in which syngas with a high CO₂ content is processed, like in the present work. In the one step DME reactor, CO, H₂ and some CO₂ are converted into DME, and methanol and water to a lesser extent. The catalyst used in the JFE process is a dual catalyst, i.e. Cu-ZnO and a kind of zeolite or alumina, suspended in a solvent (slurry reactor); one catalyst synthesizes methanol from syngas and the other dehydrates the methanol to DME. A variable amount of methanol can be fed to the reactor and converted into DME by adjusting the dual catalyst proportion [33]. Therefore, extra methanol can be converted to DME in the reactor [33]. Moreover, the Cu-ZnO catalyst is the same as (or close to) that used in the hydrocarbonylation reactor, so methyl acetate is assumed to be completely hydrogenated into methanol and ethanol in the DME synthesis reactor.

In the DME synthesis section, there are two alternatives for the processes based on DME hydrocarbonylation. The unconverted syngas from the DME conversion section can be used to produce either the amount of DME necessary for ethanol production or further DME. The latter is carried out by syngas recirculation in the DME synthesis section, or removing purge after the DME conversion section. In the DME carbonylation-based concepts, there is always a net production of DME due to the larger CO/DME ratio required. A larger CO/DME ratio causes lower methyl acetate generation compared to the case of DME hydrocarbonylation, leading to larger amounts of unconverted syngas in the DME synthesis section. In this case, the maximization of DME production results in high production of DME (the main product in terms of mass production).

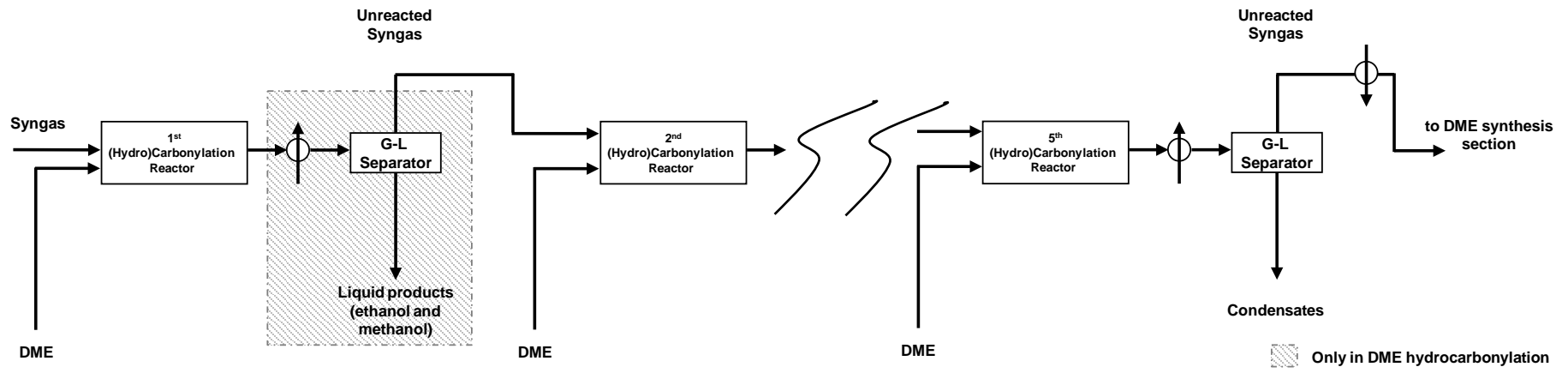


Figure 3. Configuration for the DME conversion section.

3.2.6. Product separation

The design of the product separation section depends on whether there is a DME hydrocarbonylation or a carbonylation process concept. In the first case, the liquid products are ethanol, methanol and, to a lesser extent, methyl acetate. Methyl acetate is first removed along with dissolved gases by means of a stabilizer column and recycled to the hydrocarbonylation reaction section for complete conversion to alcohols. Then, ethanol is distilled to meet fuel-grade specifications and the methanol recycled to the DME synthesis section, where it is dehydrated in the reactor by adjusting the proportion of dehydration catalyst.

In the case of alternatives using DME carbonylation, the produced methyl acetate is recovered in a stabilizer column as liquid distillate. The outlet stream from the DME synthesis reactor is condensed and CO₂ is recovered by distillation in a stabilizer column. Methanol is separated from water by distillation and recycled to the DME synthesis reactor. In concepts where DME is produced, the product stream contains around 99.0-99.5%v/v of DME, with CO₂ and methanol as the main impurities. The effluent from the DME carbonylation and the effluent from the DME synthesis reactor are cooled using the cryogenic refrigeration (CR) system.

3.3. Energy balance and integration

In most cases, the off-gas streams, mainly those coming from the DME synthesis loop purge and the vapor distillate from the DME conversion section, are enough to make the process energy self-sufficient with some power production. Only in two of the twelve cases is the power balance of the plant negative (TR-04 and TR-05 concepts) and does electricity have to be imported. For all cases, except SR-02, a combined cycle is considered for power production (see Table 3).

3.4. Process flow diagram of the cases analyzed

As examples, the process flow diagram for cases SR-01 and TR-06 are shown in Figures 4 and 5. The process flow diagrams of all process cases analyzed along with modeling details of the main equipment are presented in the Supplementary Information.

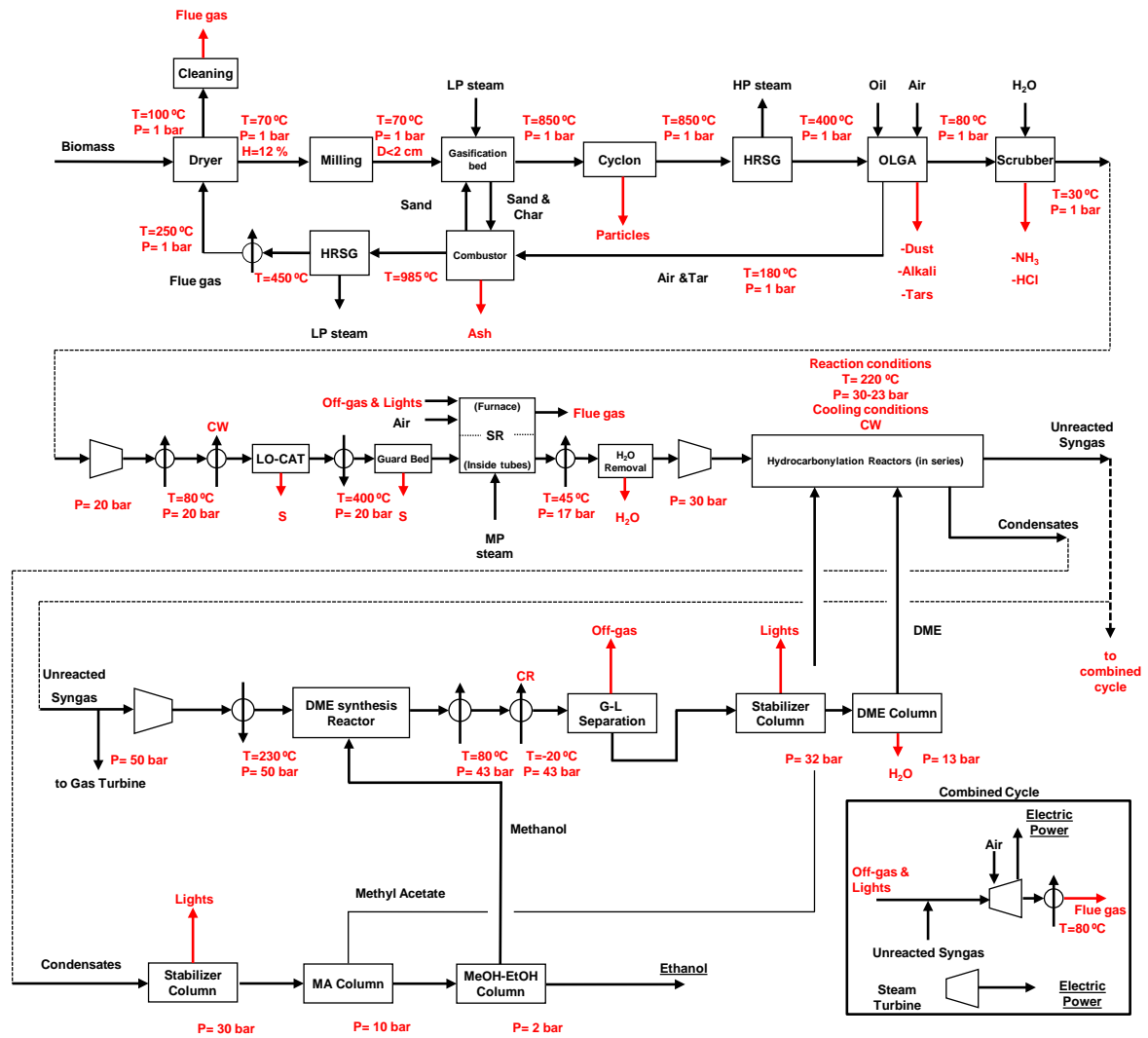
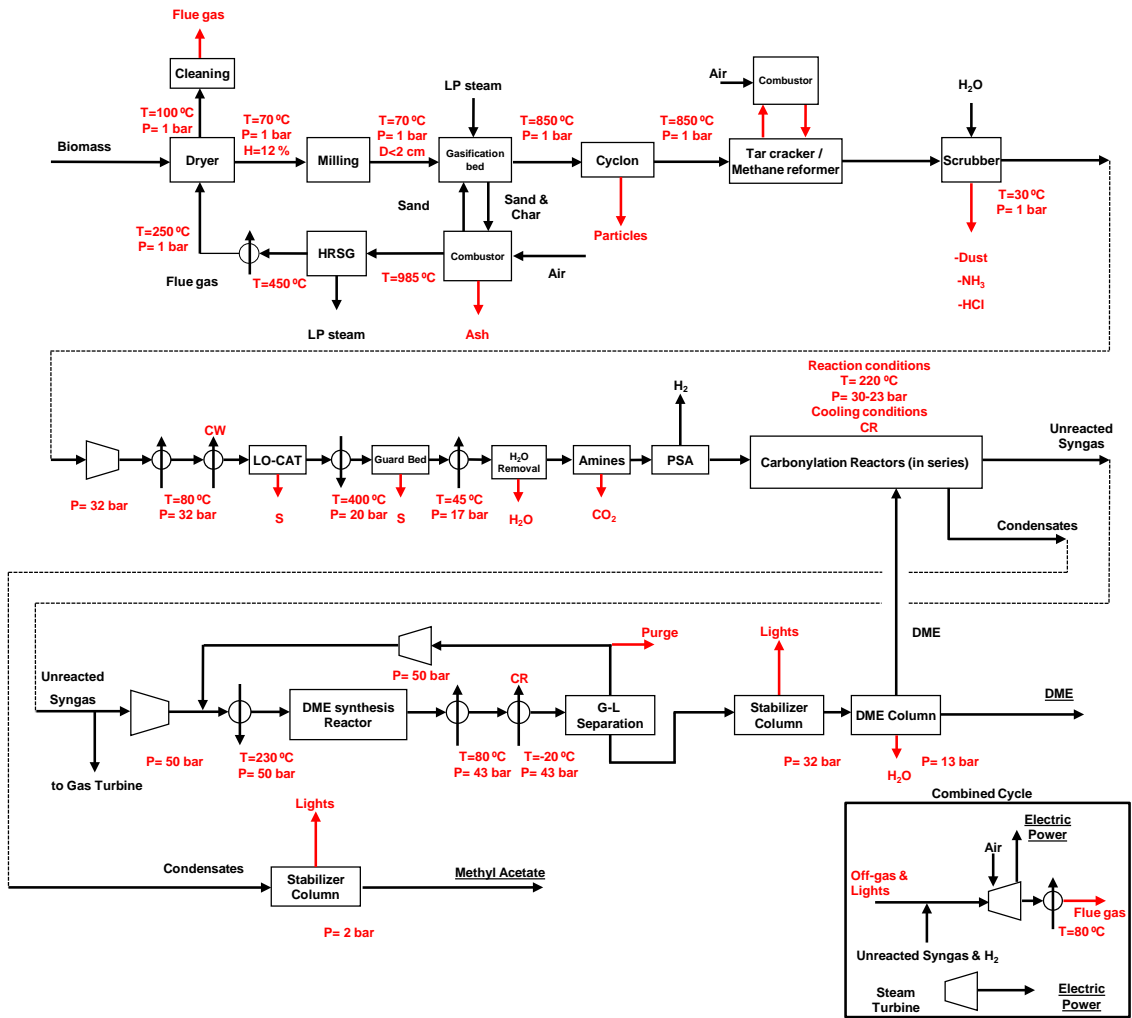


Figure 4. Process flow diagram for SR-01.

Figure 5. Process flow diagram for TR-06.



4. Further aspects on process modeling

Process concepts are modeled in Aspen Plus process simulator. The modeling parameters and assumptions of process units are presented in detailed in the Supplementary Information. Only the most important considerations are included in the following.

4.1. Thermodynamic modeling

Two thermodynamic models have been used to model the process concepts. For gasification, gas clean-up and conditioning, the DME conversion and DME synthesis reaction sections, the equation of state of Redlich—Kwong—Soave with Boston—Mathias alpha function (RKS—BM) was used. The Non-Random Two Liquids (NRTL) method with the Redlich-Kwong equation of state was used to simulate the product separation section.

4.2. Modeling and estimations of the economics of the process

The assumptions for the discounted cash flow analysis (DCFA) are shown in Table 5. The internal rate of return (IRR) of each process concept is calculated by setting the market price of products in the DCFA. Table 6 shows the market prices in the economic scenario assumed. Further information of the economic methodology is included in Supplementary Information.

Table 5. Economic assumptions for discounted cash flow analysis.

Parameter	Value
Debt/Equity	0/100%
Plant life	20 years
Depreciation (linear)	10 years
Salvage value	0 M USD
Construction period	1 year
Income tax	30%
Working capital	1-month operating costs
Land	6% TIC

Working capital and cost of land are recovered at the end of plant life.

Table 6. Commercial prices of products for the economic assessment.

Product		References
Ethanol (USD ₂₀₁₀ /L)	0.61	[34]
Methyl acetate (USD ₂₀₁₀ /L)	1.71	[35]
H ₂ (USD ₂₀₁₀ /kg)	1	[36]
DME (USD ₂₀₁₀ /m ³)	692	internal communication
Electric power	5 cUSD ₂₀₁₀ /kWh	assumed

5. Results and discussion

5.1. Energetic efficiency

Figure 6 shows the energy efficiency calculated for the 12 cases. The efficiency is defined in Eq. (1), where a transformation factor of 0.39 was assumed to translate MW_{th} to MW_e . The energy content in the various energetic vectors (products), i.e. ethanol, MA, DME, H_2 and electricity is indicated. As can be seen, electric power is a product in 10 cases, whereas there are two cases (TR-04 and TR-05) where it is imported. When extra power is required, the extra energy input is added to that of the biomass.

$$Energy\ efficiency = \frac{HHV\ of\ products\ (MW) + electricity\ generated\ (MW)}{HHV\ of\ biomass\ (MW) + \frac{electricity\ consumed\ (MW)}{0.39}} \quad (1)$$

Greatest energy efficiency is achieved by TR-02 (50.24%), where ethanol, H_2 and electric power are produced, whereas lowest energy efficiency (34.89%) corresponds to TR-03, where ethanol, DME and electric power are produced. There is no correlation between process alternatives (syngas upgrading technology, DME conversion route) and the resulting energy efficiency of process concepts.

Figure 7 shows the power sinks and sources in the alternatives analyzed. The power sinks are grouped in their corresponding process section while the power sources are directly identified. Most of the power is demanded by the clean-up and conditioning section. *Other consumptions* in the figure refers to the power demand in cryogenic refrigeration, which is the largest consumption in this group. In the power generation section a gas turbine is presented in all concepts. Thermal integration is satisfied by the steam generated within the system boundaries, including that generated in the HRSG after the gas turbine. Such a constraint makes production of extra steam impossible for power generation in SR-02 case.

Both the TR-01 and TR-06 concepts generate the highest amount of power and are also the process alternatives with the highest net electricity production. The SR-02 and TR-04 cases produce the lowest amount of power.

5.2. Economics

The economic results for all process concepts are presented below. Sensitivity analysis for some concepts, in terms of TPI and TOC, is also provided.

5.2.1. Analysis of the base case

Figure 8 shows the total operating costs (TOC) calculated for cases SR-01, ATR-03, TR-01 and TR-06, which are a representative sample of the 12 process concepts considered in this assessment. The TOC is similar for all cases, ranging from 78 (SR-01) to 90 (ATR-03)

MUSD₂₀₁₀/year. The cases based on ATR consume oxygen, increasing the TOC compared to other cases. Figure 9 shows the total plant investment (TPI) for each process alternative. The TPI ranges from 355.57 (ATR-02) to 552.74 (TR-06) MUSD₂₀₁₀. This variation is mainly due to the size of the DME synthesis and Power Island sections. The cases based on DME carbonylation produce DME, increasing the investment costs in the DME synthesis section. The process alternatives producing high amounts of electricity (TR-01, TR-03 and TR-06) also have higher TPI's due to the larger, i.e. more expensive, Power Island.

The IRR of the alternatives is shown in Figure 10. The maximum IRR corresponds to the ATR-03 (28.74%), being significantly larger than the conventional value usually assigned in similar BTL/G studies (IRR = 10%) [1, 15-18] when computing the minimum selling price of products. The highest IRR was computed for cases based on DME carbonylation. However, the internal rate of return for DME hydrocarbonylation concepts producing ethanol is around 10% for cases with SR, slightly below 10% for cases with ATR and quite low for cases with TR.

5.2.2. Sensitivity analysis

Figure 11 shows the sensitivity of the IRR to a change in the TPI of $\pm 30\%$ expected accuracy of a typical study estimate [37] for SR-01, ATR-03, TR-01 and TR-06 concepts: a representative sample. The same change ($\pm 30\%$) is used for the TOC and market price of products. The main uncertainty in the TPI is the investment cost of the gasifier and reforming technology, whereas in the TOC it is the cost of the biomass. For the market price of products, uncertainty is hard to assess accurately. Hence, it has been assumed to range equal as the TPI and TOC.

The trend is similar for both the TPI and TOC: the impact on the internal rate of return amounts to a maximum variation of +12/-10 points. The impact is similar for the market price of each product. Nevertheless, more volatility might be expected for the commercial price of products, increasing the impact on the internal rate of return.

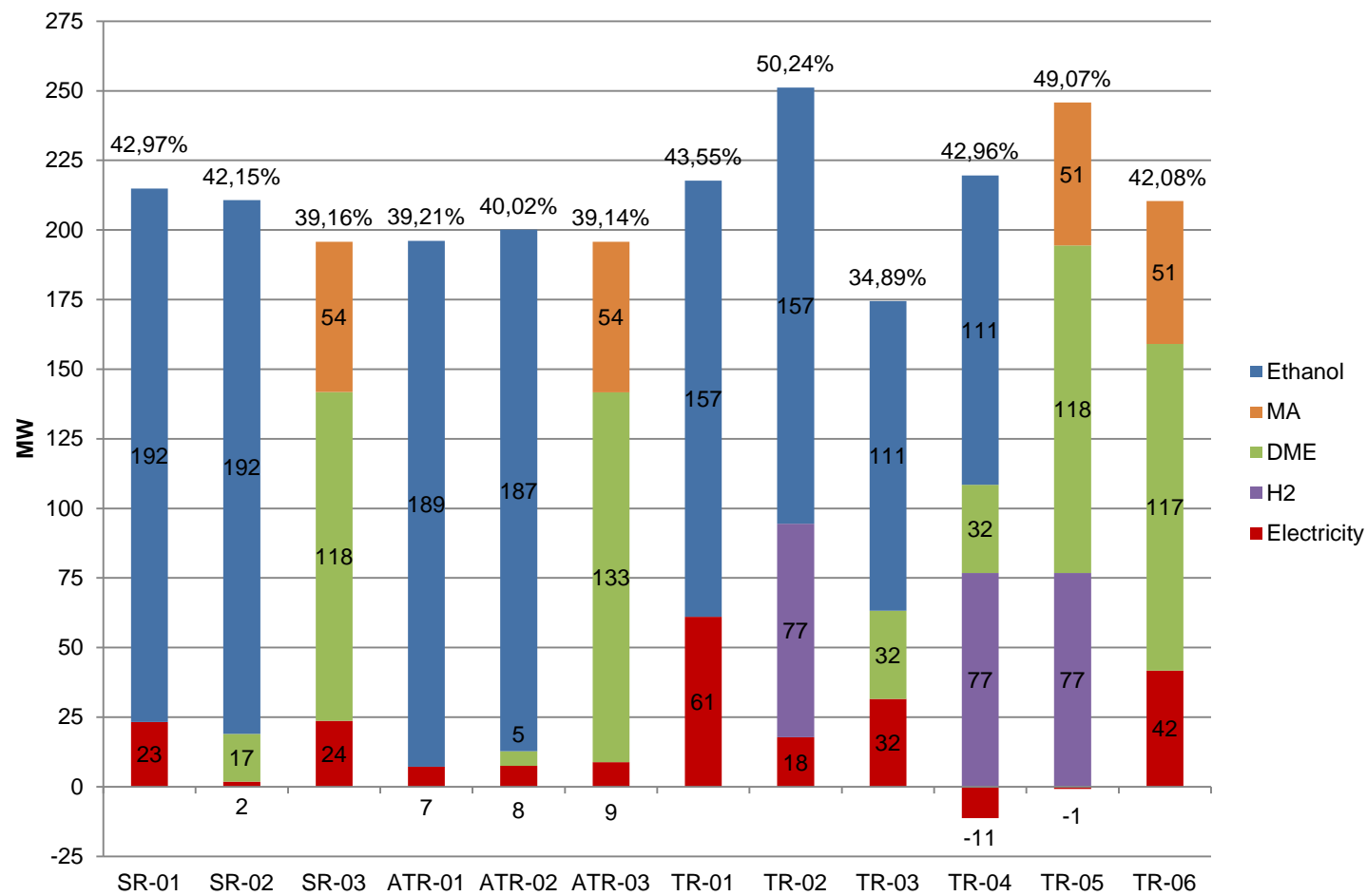


Figure 6. Global energy efficiency (%HHV) and energy content to products (in MW) for each process concept.

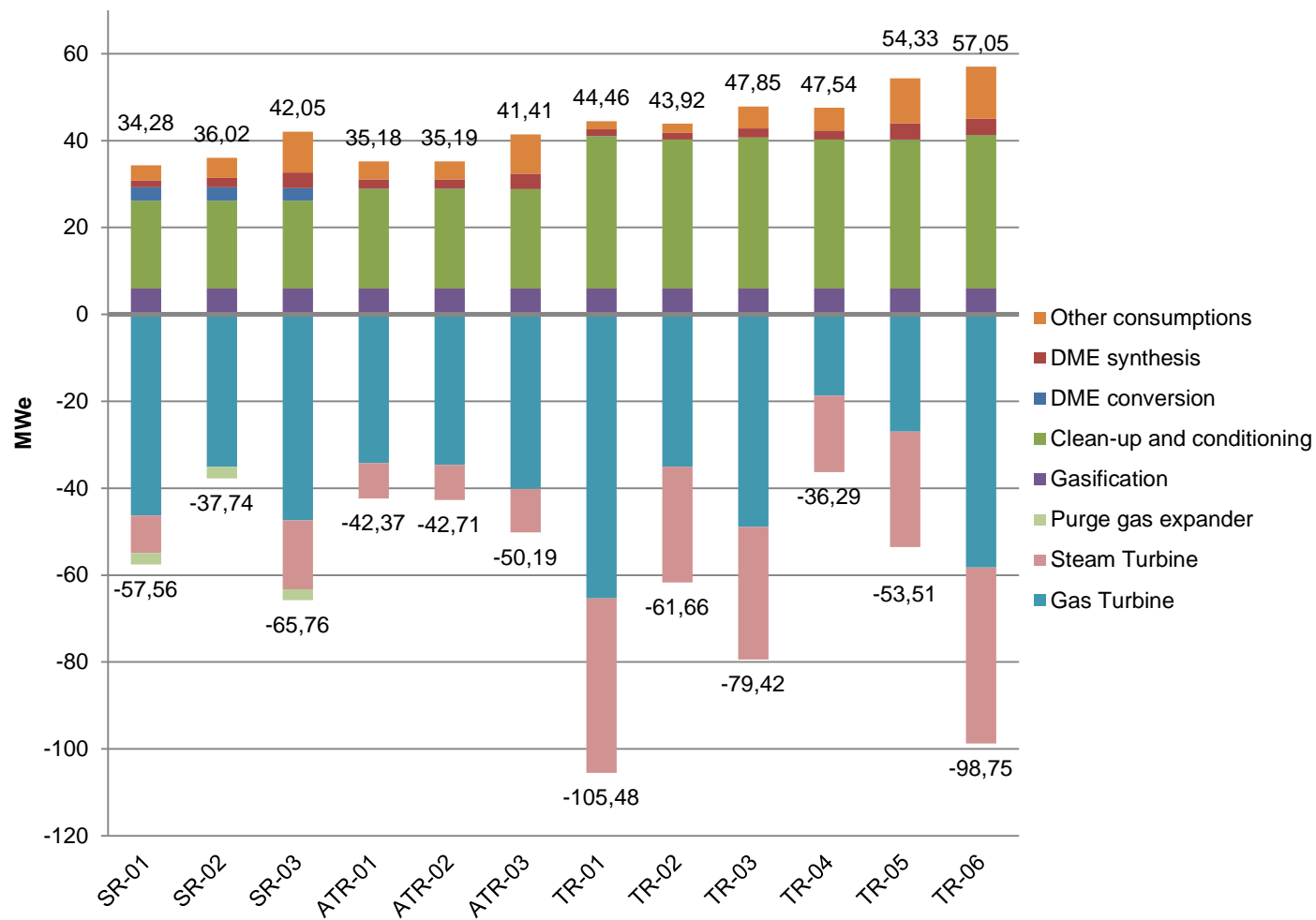
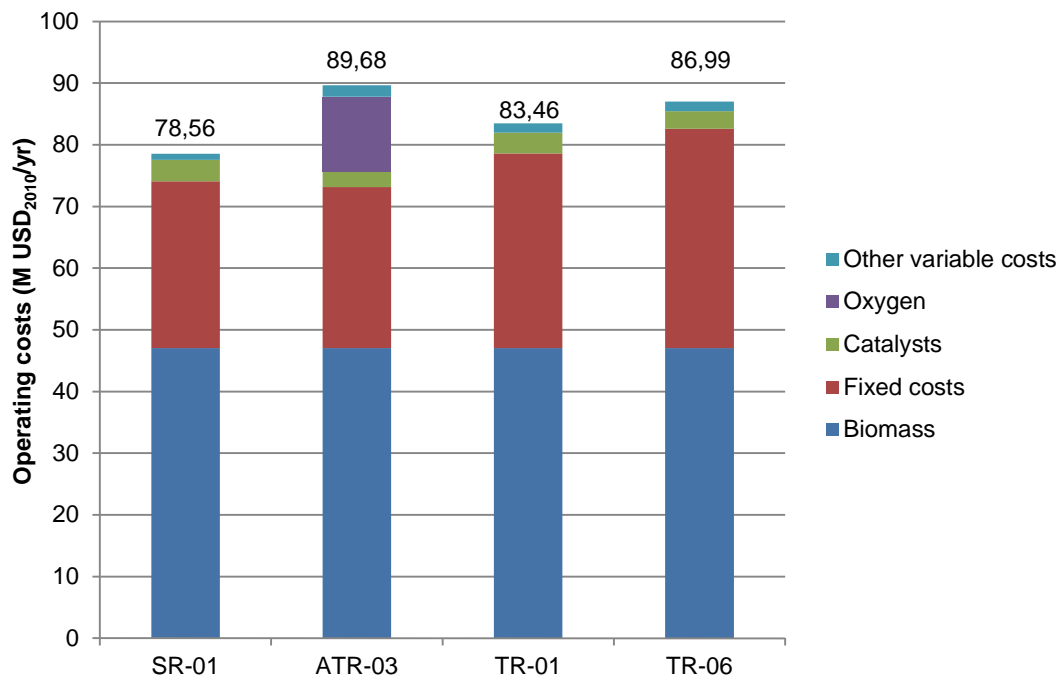


Figure 7. Power consumption and generation for the cases analyzed.

Figure 8. TOC for some assessed process concepts.



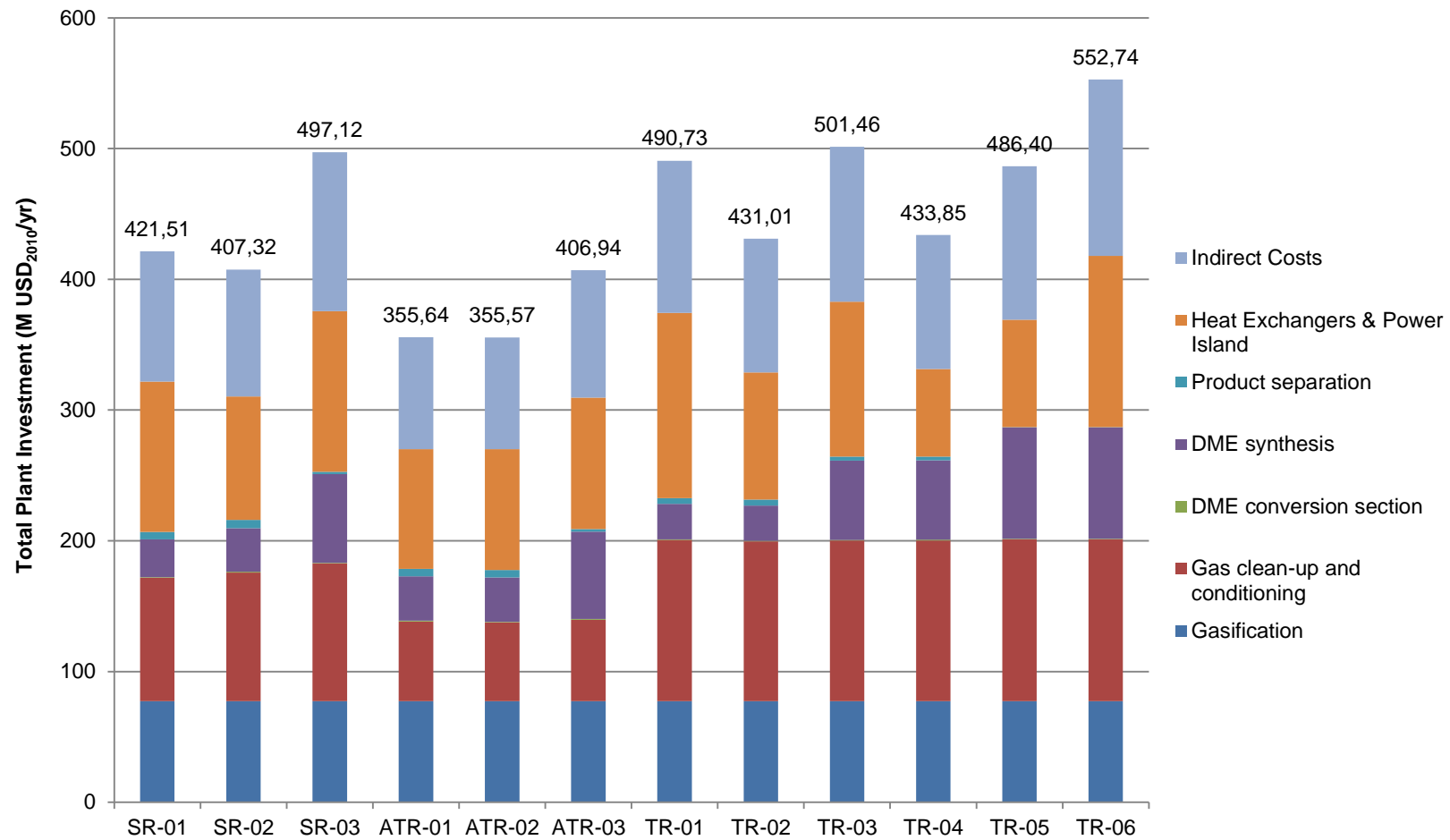


Figure 9. TPI for each assessed process concept.

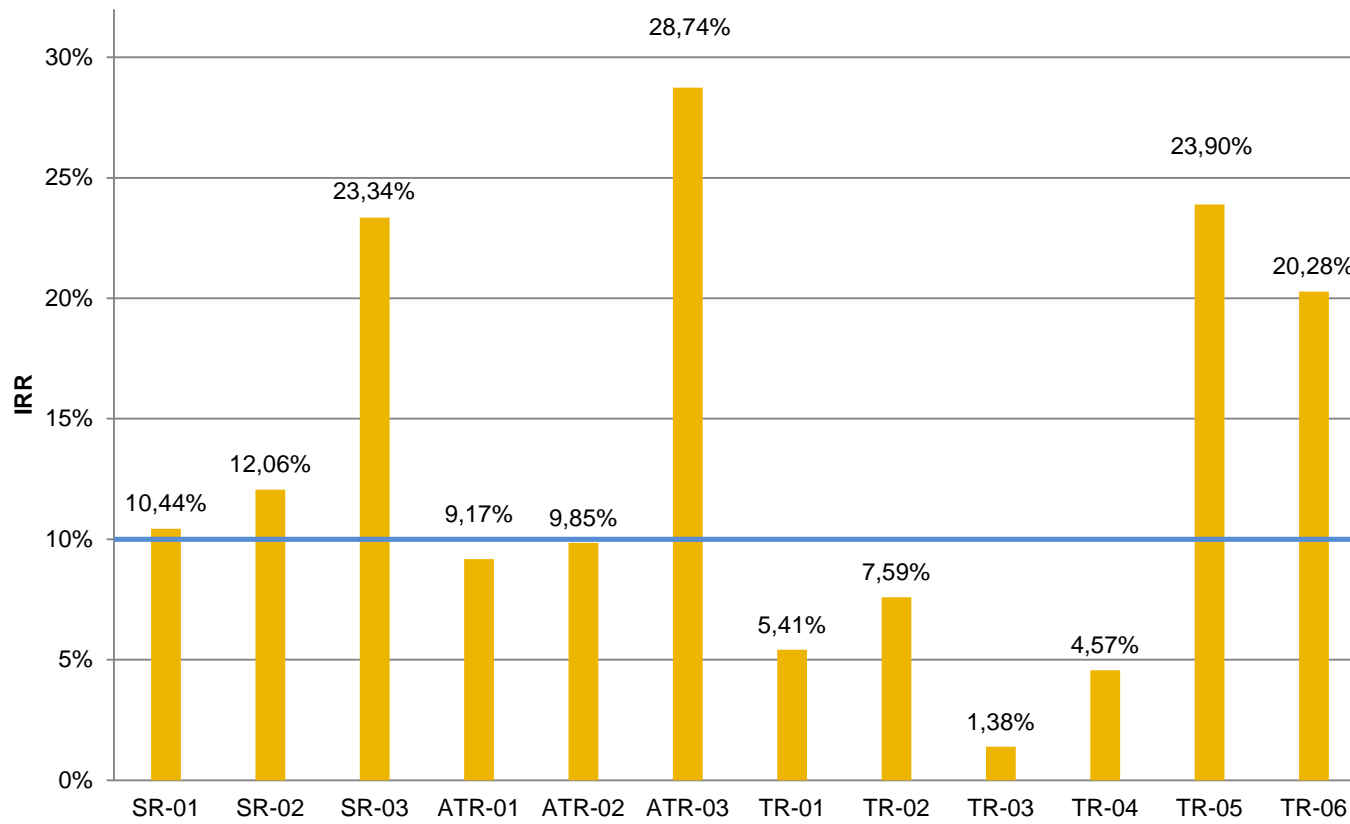


Figure 10. Internal rate of return of each process concept.

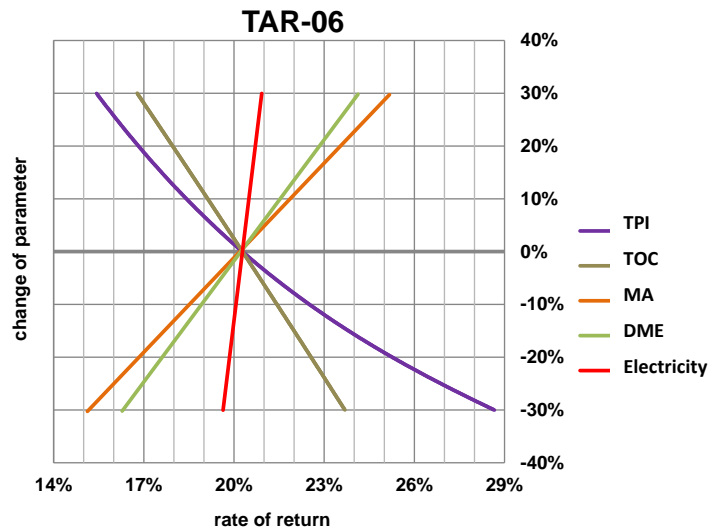
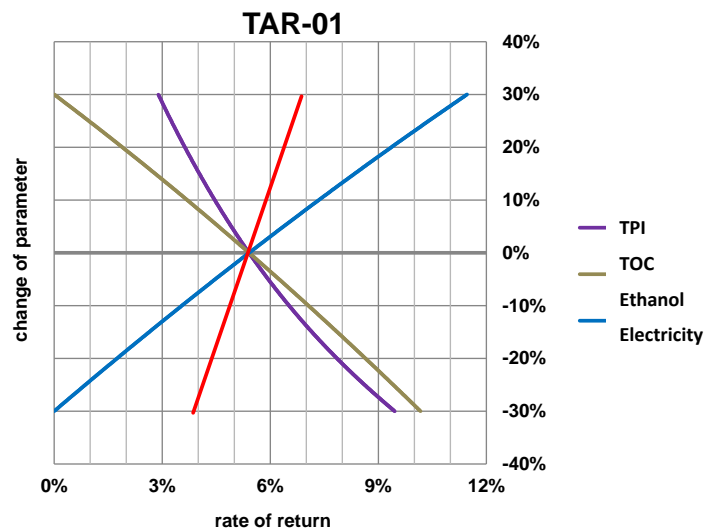
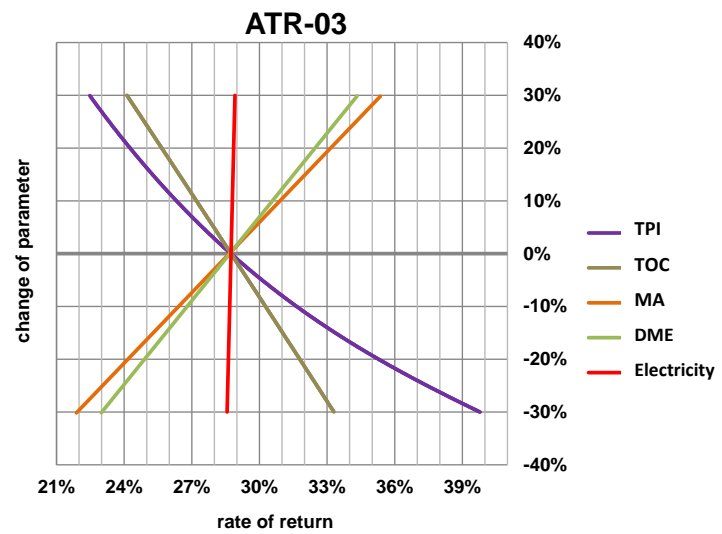
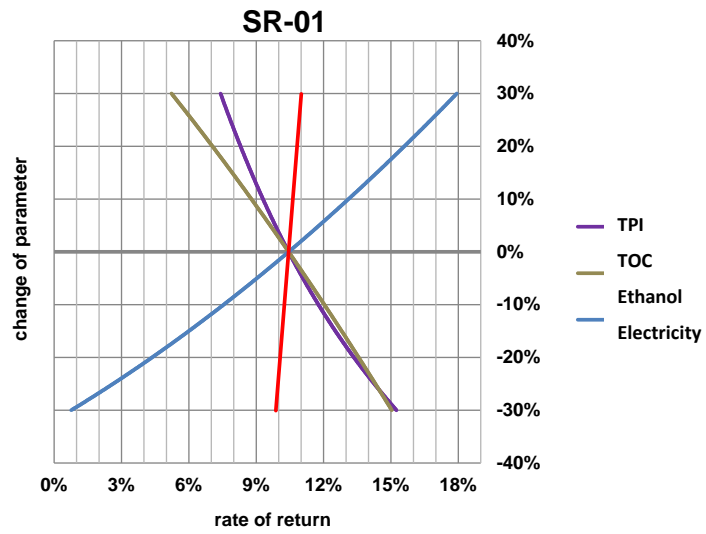


Figure 11. Sensitivity analysis for some assessed concepts.

5.3. Discussion

In this paper, special attention to both energetic efficiency and rate of return is given as they are critical for a comprehensive comparison of BTL/G processes. The feasibility analysis of new production processes requires evaluation of these indicators in order to select the most promising options. The energetic efficiency enables the comparison with competing BTL/G or analogous petrochemical processes. In this work, the resulting energetic efficiencies are close or even greater than those reported in similar BTL/G assessments [1, 15, 16]. However, the energetic efficiencies of dedicated DME [38-40] and methanol [40, 41] production processes are slightly higher than our best biorefinery concept. The lower energetic efficiency obtained in this work is justified by the additional conversion steps necessary to transform DME into derived-products. The rates of return obtained in the cases of DME carbonylation reveal that the combination of high biomass price and methyl acetate selling price does not make critical the TPI of the plant, so economic feasibility of the process can be achieved. These obtained rates of return differ significantly from previous BTL/G studies. In the cases of DME hydrocarbonylation the high biomass price and moderate commercial price of ethanol makes the TPI critical, so the feasibility of the process is questionable. Furthermore, the TPI is very sensitive to variations of the ethanol price.

6. Conclusions

Twelve process concepts based on DME as an intermediate are technoeconomically assessed, considering both the carbonylation and hydrocarbonylation of DME for commercial purposes. The assessment includes biomass pretreatment, gasification, syngas upgrading, DME synthesis and conversion, product separation and heat and power integration. Process alternatives considered in this study (Table 3) are made according to current and future market development for both technical viability and economic feasibility of a thermochemical biorefinery at medium term.

The results of this study establish that a thermochemical biorefinery based on DME as an intermediate achieves similar energy efficiencies to other BTL/G studies [16, 19, 23, 24, 26, 28], i.e. from 35 to 60%. The calculated TPI and TOC are also close to those obtained using the same techno-economic procedure and economic data [15, 17]. For the market price of products the internal rate of return is always above 20% for process concepts based on DME carbonylation. The largest rate of return was 28.74%, corresponding to the cases where methyl acetate, DME and power are produced (ATR-03 in Table 3). For the concepts based on DME hydrocarbonylation, the rate of return is lower, but still competitive if steam reforming or autothermal reforming is selected. The sensitivity analysis shows that the impact of uncertainties in TPI, TOC and market prices amounts to a maximum variation of +12/-10 points in the internal rate of return.

Despite the inherent complexity of a thermochemical biorefinery based on DME as an intermediate, similar profitability and energetic efficiency to other BTL/G processes producing a single product is achieved. Therefore, the concept analyzed is a promising route for biomass-derived fuels and chemical production.

Further work is needed to complement the analysis made in the present article, including: life cycle assessment, study of potential carbon footprint reduction, the possibility of extra revenue due to avoided greenhouse-gas (GHG) emissions, and optimization of the DME conversion reaction conditions at laboratory scale.

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