Technoeconomic assessment of lignocellulosic ethanol production via DME hydrocarbonylation

Abstract

In this study, a new thermochemical route to produce lignocellulosic ethanol based on DME (dimethyl ether) hydrocarbonylation is proposed and economically assessed. The process is designed and evaluated using current kinetic laboratory data for hydrocarbonylation reactions. Only available technologies or those expected to be available in the short term are considered for the process design, which involves biomass pretreatment and gasification (indirect circulating fluidized bed), gas clean-up and conditioning, methanol synthesis, DME production by methanol dehydration and DME hydrocarbonylation. The process is designed to be both energy self-sufficient and electrical energy neutral. For a plant size of 2140 dry tonnes/day of wood chip (500 MW HHV) the minimum selling price of ethanol (for a 10% rate of return and a biomass price of 66 \$/dry tonne) ranges from 0.555 to 0.592 USD 2010/L of automotive grade ethanol with fixed capital costs between 333 and 352 M USD 2010. Energy efficiency of biomass to ethanol ranges from 44.35 to 45.53% (high heating value basis). These results compare favorably with the "state of the art" production of ethanol via biochemical pathway from lignocellulosic biomass, revealing that the DME hydrocarbonylation route is a promising one that could be cost-competitive in the near future.

Keywords: Ethanol; 2nd generation biofuels; Thermochemical; Biomass; Economics; Indirect routes

1. Introduction

Bioethanol is increasingly used as a transportation fuel in USA, Brazil and Europe. It can be used pure in vehicles with modified internal combustion engines (ICEV) or blended with gasoline in regular ICEV. Nowadays, most bioethanol is produced by first generation processes based on fermentation technologies for sugar and starchy crops. However, these crops have some drawbacks: a high value for food application and low sugar yield per hectare. Thus, currently, suitable processes for lignocellulosic biomass are being developed under the name "2nd generation bioethanol processes".

This abundant and relatively cheap biomass can be converted to ethanol by hydrolysis and fermentation (bio-chemical pathway) but also by thermochemical processing, i.e. gasification of biomass to synthesis gas (syngas) followed by catalytic synthesis or syngas fermentation. Technoeconomic studies of the direct synthesis of alcohols from syngas produced by biomass gasification have been carried out by several researchers, either based on patented catalysts [1] or expected performance of these catalysts in the future [2, 3, 4]. From the results of this research, it is clear that significant development of current mixed alcohol catalysts is needed, in terms of conversion and selectivity to ethanol, to make the process economically feasible. Indirect synthesis processes (indirect routes) could be an interesting option if they were able to achieve higher ethanol productivity so as to outweigh their inherently greater complexity.

Routes to make ethanol from syngas, through one intermediate, have been reviewed recently by Subramani [5]. This review discusses three indirect routes to ethanol: the methanol bimolecular reaction route, the methanol homologation (reductive carbonylation) route and the acetic acid route (ENSOL process) [6]. Other current indirect routes not reviewed are: indirect acetic acid route [7], Enerkem's process via methyl acetate [8, 9], dry ethanol process [10] and ethanol via dimethyl ether (DME) hydrocarbonylation [11]. Enerkem Inc. has recently developed the ethanol via methyl acetate process with a demonstration plant and two commercial plants in project or under construction [8].

In this paper, a conceptual design of a thermochemical process for the production of ethanol via DME hydrocarbonylation route is developed and economically assessed by the ASPEN PLUS process simulator. The process makes use of commercial methanol and DME synthesis technologies. No commercial DME hydrocarbonylation reactor exists today but its development

is not expected to be difficult as hydrocarbonylation reaction is slightly exothermic at mild conditions (15 bar, 220 ºC), and only heterogeneous catalysts are involved.

The paper is organized as follows. First, a description of the DME hydrocarbonylation chemistry is presented which includes a short discussion of catalysts, reaction conditions and experimental kinetic data found in the literature [11, 12]. Then, the conceptual process design and modeling is described including the main design assumptions and parameters. Finally, the performance of the process is calculated for different conditions in the DME hydrocarbonylation reactor, which is modeled using the experimental kinetic data. Results of the simulation are used to assess and compare the economics of the process for each case.

2. Ethanol via DME Hydrocarbonylation Route

Recently, a new route to make ethanol from DME and syngas has been proposed [11, 12]. The innovation resides in the use of a dual catalytic bed reactor of H-Mordenite and Cu/ZnO. DME reacts with CO from the syngas to form methyl acetate in the presence of H-Mordenite catalyst (Eq. 3). Formed methyl acetate is hydrogenated to ethanol and methanol by means of the Cu/ZnO catalyst (Eq. 4).

H-Mordenite is a kind of acid zeolite that selectively catalyzes the carbonylation of DME to methyl acetate at a relatively low temperature and pressure (15 bar, 220 ºC). A great excess of CO is necessary to achieve appreciable productivities of methyl acetate due to low catalyst activity, but there is a potential for significant improvement [13]. For methyl acetate hydrogenation several metal-based catalysts could be employed [9, 14, 15, 16], such as the Cu/ZnO catalyst used in reported DME hydrocarbonylation experiments [11, 12, 17].

Table 1 shows the results obtained by Tsubaki et al. [11] using a single reactor comprised of a H-Mordenite bed in series with a Cu/ZnO bed. This single reactor produces ethanol from DME, CO and H_2. The high conversion of DME is probably caused by shifting of the carbonylation reaction by "in situ" hydrogenation of methyl acetate as soon as it is produced [11]. Table 1 also shows the effect of the CO/DME ratio on the per-pass conversion and selectivities to ethanol, methanol, methyl acetate and CO_2. As this ratio increases from 10:1 to 49:1 both per-pass conversion and ethanol selectivity increases. Thus, from a process design point of view, there would be a trade-off between ethanol productivity and syngas recirculation costs. This trade-off is economically analyzed in this paper by simulating the process for the five CO/DME ratio cases included in Table 1.
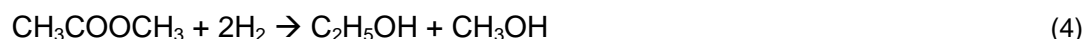
Case Study	P (bar)	T (ºC)	H_2/CO molar ratio	DME Conversion	Selectivity of MeOH	Selectivity of EtOH	Selectivity of Methyl Acetate	Selectivity of CO_2
Ratio 10:1	15	220	1	48%	45.0%	38.0%	6.5%	10.5%
Ratio 20:1	15	220	1	55%	44.5%	39.0%	6.5%	10.0%
Ratio 30:1	15	220	1	78%	44.5%	40.5%	6.5%	8.5%
Ratio 40:1	15	220	1	83%	46.5%	41.5%	5.0%	7.0%
Ratio 49:1	15	220	1	98%	47.5%	46.0%	2.5%	4.0%

3. Process Design and Modeling

3.1. Conceptual design

Figure 1 shows the conceptual block diagram of the process. Biomass is first converted to syngas in an atmospheric circulating fluidized bed gasifier. The producer gas is cleaned-up and conditioned in order to meet the requirements of the catalysts used in the reactor network. The configuration of the reactor network is largely dictated by the way in which DME is produced in the plant. DME for hydrocarbonylation can be produced from syngas by direct synthesis or indirectly by first synthesizing methanol which is subsequently dehydrated. Based on material and energy integration issues for this specific process, the second option has been selected as it allows for the use of the dehydration reactor to convert methanol co-produced in the hydrocarbonylation reactor back to DME in order to increase ethanol production. Thus, the synthesis reactor network comprises three catalytic reactors.

As a result of the process configuration selected, the whole indirect route comprises the following set of reactions (in order of process design):

$$CO + 2H_2 \rightarrow CH_3OH \tag{1}$$
$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{2}$$
$$CH_3OCH_3 + CO \rightarrow CH_3COOCH_3 \tag{3}$$
$$CH_3COOCH_3 + 2H_2 \rightarrow C_2H_5OH + CH_3OH \tag{4}$$

The global reaction of the direct synthesis of ethanol being:

$$4H_2 + 2CO \rightarrow C_2H_5OH + H_2O \tag{5}$$

The high global selectivity to ethanol [12] makes this indirect route very appealing, especially compared to the direct synthesis route. However, a drawback of the analyzed route is the high excess of reactant (CO) needed to achieve a relatively high per-pass conversion of DME.

Another advantage of this indirect route is that separation of ethanol-water mixtures is not necessary as water is not co-produced with alcohols in the same reactor, which occurs in the direct synthesis of ethanol. This results in energy savings for distillation because the dehydration of ethanol is not necessary. Water is only generated in the DME synthesis reactor but this is not a problem as water can be easily separated from DME before feeding DME to the hydrocarbonylation reactor, preventing deactivation of H-Mordenite by water [11, 12, 13]. The methyl acetate produced in the hydrocarbonylation reactor is recycled to the reactor where it is assumed to be hydrogenated to methanol and ethanol.
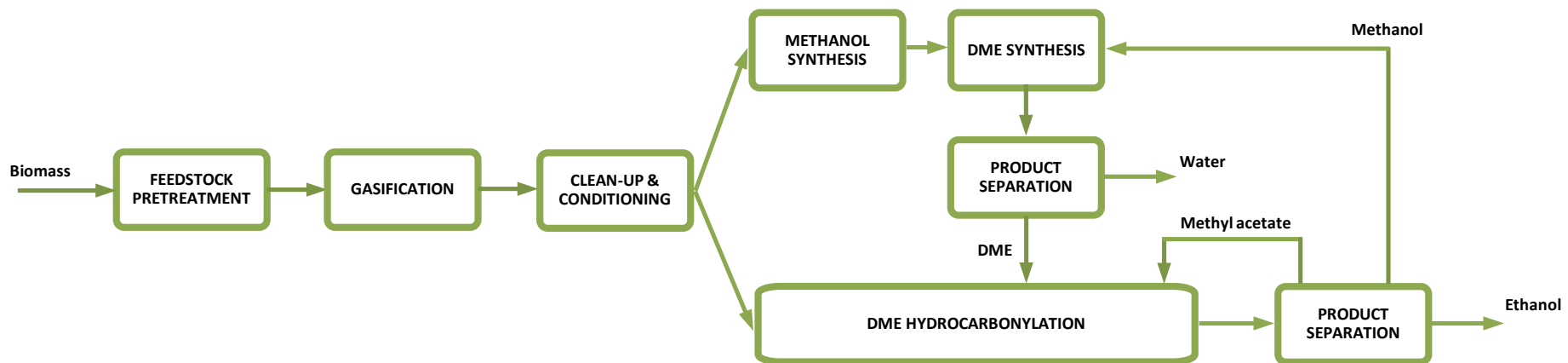
Figure 1. Scheme of ethanol via DME hydrocarbonylation route.

3.2. Process description and modeling

Figure 2 shows a block diagram of the process. As a design basis, a plant size of 2140 dry tonnes/day of poplar chip (500 MW_{HHV}) was selected. This plant size is very similar to that selected in other BTL plant assessments [2, 3, 4, 18], allowing for direct comparison with results obtained in these studies. Below, each process area is briefly described and the modeling approach is presented.

Figure 2. Process block diagram.

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3.2.1. Feedstock pretreatment

Poplar chip is delivered to the plant gate with 30 wt% moisture and dried in a rotary dryer, where moisture content is reduced to 12 wt% with combustion gases from the indirect circulating fluidized bed gasifier. The combustion gases are previously cooled down to 450ºC in an HRSG, where HP steam is generated. This temperature is selected in order to obtain a flue gas temperature of 150°C at the outlet of the rotary dryer, ensuring good dispersion of the plume. Dried poplar chips are sent to a hammer mill for size reduction under 4 cm. The ultimate analysis of poplar chips feedstock is given in Table 2.

3.2.2. Gasification

Gasification can take place at different pressures, by direct or indirect heating and oxygen or air. For the synthesis of liquid fuels a non-diluted syngas with nitrogen is preferred. This leads to three gasifier alternatives: (a) a pressurized entrained flow gasifier operated with oxygen, (b) a pressurized or atmospheric CFB (circulating fluidized bed) operated with oxygen/steam and (c) an atmospheric-pressure indirect CFB gasifier operated with air/steam. An atmospheric indirectly-heated CFB is selected because it does not require an Air Separation Unit (ASU), which would consume a significant amount of power [2]. The gasifier is modeled using correlations (a non-equilibrium model) based on experimental data from the Battelle Columbus Laboratory gasifier as reported by [19]. The gasifier performance for the selected operating conditions is shown in Table 3.

3.2.3. Gas Clean-up and Conditioning

The 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 downstream. First, particulates are partially removed by high-temperature cyclones. Next, tars and the rest of particulates are removed using a wet scrubbing system with organic dissolvent (OLGA^{TM}) [20]. Collected tars are recycled to the combustor of the indirect CFB gasifier. Nitrogenous compounds, alkalis and HCl are removed by consecutive scrubbers. The resulting stream is compressed to 17 bar and desulfurized in a liquid phase oxidation process (LO-CAT) where H_2S is oxidized to elemental sulfur. The LO-CAT process was selected because it is appropriate to treat gases with low H_2S content and does not remove CO_2, which is needed in the steam reformer as explained below [21, 22]. The concentration of H_2S and total organic sulfur compounds in the outlet stream is decreased to ppbv levels by hydrogenation of organic sulfur compounds and further H_2S removal in a Co-Mo/ZnO dual bed. This guard bed also hydrogenates olefins to parafins which are easier to reform. At the inlet of the Co-Mo/ZnO dual bed a fraction of the partially cleaned gas is diverted to the power plant in order to satisfy the energy self-sufficient criteria.

The desulfurized syngas enters a steam methane reformer (SMR) where methane and light parafins are converted into syngas. CO_2 must be fed into the steam methane reformer in order

to get a H_2/CO molar ratio equal to 1 at the hydrocarbonylation reactor inlet (H_2/CO ratio of hydrocarbonylation experiments, Table 1). However, that would require a large recirculation of CO_2 from the Amine unit located in the hydrocarbonylation loop. There is an economic trade-off between large-scale CO_2 recycle and performance of the hydrocarbonylation reactor, which cannot be evaluated due to the lack of experimental kinetic data for different H_2/CO ratios. Relatively low CO_2 recycle was considered resulting in H_2/CO ratio between 1.2 and 1.55 at the hydrocarbonylation reactor inlet. The implications of this decision are explained in the DME hydrocarbonylation loop section. The reformed gas is dehydrated in a molecular sieve, preventing the presence of water in the DME hydrocarbonylation reactor. A fraction of the reformed syngas is sent to the hydrocarbonylation loop while the rest is sent to the methanol synthesis reactor. The split fraction to the hydrocarbonylation reactor ranges from 0.4 to 0.6 depending on the desired CO/DME operating ratio.

Table 2. Ultimate analysis of biomass feedstock (poplar chip).

Component	% wt, dry basis
Carbon	50.90
Hydrogen	6.05
Oxygen	41.92
Nitrogen	0.17
Sulfur	0.04
Ash	0.92
Moisture	30% wt
HHV (d.b)	20.18 MJ/kg

Table 3. Gasifier operating parameters, exit gas composition and efficiency.

Gasifier Performance	
Pressure	1.5 bar
Temperature	900 ºC
Steam (2 bar, 140ºC)/dry Biomass ratio	0.4
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_2O	43.43
CH_4	08.43
H_2S	184 ppm
NH_3	0.18
Tars	0.15
Lights	2.70

3.2.4. Methanol synthesis

The syngas feed to the methanol reactor is compressed to 50 bar and heated to 235°C. There is a wide variety of commercial methanol synthesis technologies that can be selected for this application. However, this analysis is based on a Liquid Phase Methanol (LPMEOH) reactor modeled with data from the Kingsport LPMEOH™ CCT Project [24, 23]. This slurry type reactor is able to process CO rich syngas and achieves high per-pass conversion to methanol, so that no recirculation of unconverted syngas is needed. Besides, the liquid phase methanol reactor is flexible in terms of feed composition which is advantageous as the H_2/CO ratio of the reformed syngas only needs to be adjusted to satisfy the requirements of the hydrocarbonylation reactor. The once-through operation allows enough methanol production for the DME synthesis step. The output stream of the methanol reactor is cooled down to 45°C for methanol recovery but also most of the water co-produced. The off-gas stream from the gas-liquid separator comprises unreacted syngas, and small quantities of methanol, DME and traces of water. The off-gas is expanded down to the hydrocarbonylation reactor pressure in a turboexpander, and then sent to the hydrocarbonylation synthesis loop.

3.2.5. DME hydrocarbonylation loop

The feed to the hydrocarbonylation reactor is a mixture of five gas streams: (a) clean and conditioned syngas fraction from SMR, (b) off-gas from the methanol synthesis area, (c) unconverted syngas from the hydrocarbonylation reactor, (d) DME from the methanol dehydration reactor and (e) recycled by-products of the hydrocarbonylation reactions (mixture of methanol/methyl acetate). Streams (d) and (e) contain small amounts of methanol and ethanol. In the hydrocarbonylation reactor it is widely considered that recycled methanol and ethanol behave as inerts while recycled methyl acetate is completely hydrogenated [9, 11, 12, 14, 15, 16]. As previously mentioned, in the simulations, the H_2/CO ratio at the inlet of the hydrocarbonylation reactor (see Table 4) is larger than the H_2/CO ratio of the hydrocarbonylation experiments (Table 1). Based on a recent study [25], the H_2/CO ratio does not affect the conversion of DME in the carbonylation bed. However, a larger H_2/CO ratio will probably result in higher methanol production from CO in the hydrogenation bed. This is not a critical problem as methanol is recycled and converted back into DME and the global productivity will not dramatically change. Nonetheless, it is recognized that a larger methanol recycle will also increase capital and operating costs. Therefore, there is an optimum setting for the H_2/CO ratio which minimizes the total cost of recycling CO_2 to the SMR and methanol to the dehydrator. The optimum H_2/CO ratio cannot be determined due to the lack of hydrocarbonylation experiments at different H_2/CO ratios. As an approximation, we have assumed that the product distribution does not change with the H_2/CO ratio. Regarding the configuration of the reactor, the simulations show that the adiabatic ΔT is close to common methanol synthesis reactors, so similar reactor designs would be suitable.

The reactor effluent is cooled down to 35ºC with cooling water. A knock-out vessel is used to separate unconverted syngas and DME from condensed products with reasonable ethanol recovery (nearly 80%). In order to avoid a build-up of CO_2 concentration in the synthesis loop an amine scrubber using monoethanolamine (MEA) is employed. However, a purge is necessary in order to prevent methane build-up in the hydrocarbonylation loop (10% v/v methane as design limit).

3.2.6. Products separation

The condensate from the gas-liquid separator of the hydrocarbonylation loop is processed in a stabilizer column with a partial condenser. The vapor distillate which contains the dissolved gases (mainly CO_2 and CH_4) is recycled to the burners of the SMR. The liquid distillate contains 98% of the incoming methyl acetate diluted with methanol, ethanol and traces of DME. This stream is recycled to the hydrocarbonylation reactor to achieve total methyl acetate conversion. The bottom stream recovers 95% ethanol and 80% methanol. This stream is depressurized and enters into a column distillation where methanol is recovered as distillate while ethanol is recovered as bottom stream. Methanol is sent to the dehydration reactor to produce more DME. The ethanol product satisfies ASTM specifications for automotive spark-ignition engines.

3.2.7. Methanol dehydration and byproducts recycle and conversion

The methanol synthesized in the LPMEOH reactor and co-produced in the hydrocarbonylation reactor are dehydrated to DME in a fixed-bed reactor. The dehydration reaction can take place on different solid-acid catalysts such as γ-alumina, modified-alumina with silica and phosphorus, Al_2O_3–B_2O_3 and molecular sieve materials (chabazites, mordenites, SAPOs, etc.), in a temperature range of 250–400 ºC and pressures up to 20 bar [26, 27]. In this study, we have selected modified γ-alumina, which has shown good stability and is widely employed by companies such Air Products and Toyo Engineering Corporation. For this analysis, we used typical Toyo dehydration conditions, i.e. conversion of 85% and almost 100% selectivity to DME [27]. The gas outlet stream from the dehydration reactor is cooled down and fed to a distillation column to obtain a DME rich overhead stream and an aqueous bottom stream. This stream is sent to the water treatment area which is not modeled here but is included in the economic assessment.

3.2.8. Energy Integration and Balance

As previously mentioned, all cases were designed to be both energy self-sufficient and "electrical energy neutral". First, the heat exchanger network is designed manually by matching close hot and cool streams whenever possible. A minimum temperature difference of 20 ºC, 30ºC and 40 ºC are considered for liquid-liquid, liquid-gas and gas-gas heat exchanges, respectively. The main heat sources for high pressure steam generation are the outlet of SMR, raw syngas from the gasifier and the flue gas from the char combustor. The power demands of the plant are completely satisfied by diverting some cleaned-up syngas to a combined cycle as

shown in Figure 2. The main heat sinks of the process are the boilers of the distillation columns and amine unit, and hydrocarbonylation loop preheaters.

The modeling of process units is summarized in Table 4.

Table 4. Modeling of main process units.

	Parameter	Value	
Heat Exchangers	Pressure drop	3 psi	
Pumps	Mechanical Efficiency	0.90	
Compressors	Isentropic efficiency	0.78	
	Max. pressure ratio	3.5	
Process Turbines	Isentropic efficiency	0.72	
Gas Turbine	Isentropic efficiency	0.90	
	Pressure	49 bar	
	Temperature	250ºC	
	CO per-pass conversion	30.76%	
Methanol reactor	CO_2 per-pass conversion	8.90%	
[23, 31]	Selectivity to MeOH	89.15%	
Modeled as a RStoic	Selectivity to H_2O	10.57%	
	Selectivity to DME	0.14%	
	Selectivity to methane	0.14%	
	H_2/CO ratio	1.70	
	Pressure drop	3.3 bar	
Hydrocarbonylation reactor	H_2/CO ratio (for each CO/DME ratio)	10:1	1.57
		20:1	1.52
		30:1	1.34
Modeled as a RStoic (see Table 1 for conversion, selectivities and operating conditions)		40:1	1.53
		49:1	1.29
	Pressure drop	10 psi	
	Pressure	20.2 bar	
	Temperature	320 ºC	
	MeOH per-pass conversion	85%	
Methanol Dehydration reactor	EtOH per-pass conversion	80%	
[27]	Selectivity to DME	100%	
	Selectivity to C_2H_4	100%	
Modeled as a RStoic	% v/v ethanol in feed	0.2%	
	% v/v H_2O in outlet stream	44.9%	
	Pressure drop	10 psi	

3.3. Thermodynamic Modeling

Two thermodynamic models have been used for process simulation. For gasification, and gas clean-up and conditioning areas, the equation of state of Redlich–Kwong–Soave with Boston–Mathias alpha function (RKS–BM) is employed, whereas the NRTL–RK model is employed in methanol synthesis, DME hydrocarbonylation, methanol dehydration and product separation areas. These thermodynamic models for process simulation were chosen according to recommendations from the literature [28] and ASPEN PLUS documentation. For the NRTL model, binary parameters for DME-water, DME-methyl acetate and DME-ethanol mixtures are taken from the literature [29, 30].

4. Process Economics

Results from the process simulations were used to estimate capital and operating costs. Purchase costs for equipment (PEC) are taken from published BTL studies and vendor quotes. First, the purchase costs are scaled and the effect of inflation is corrected by using the CEPCI (Chemical Engineering Plant Cost Index) index. Then, the installed equipment cost is calculated by multiplying the purchase cost by an installation factor. If the installation factor is unknown it is assumed 2.47 according to Table 5. Thus, the total installed cost (TIC) is calculated by adding up the cost of the individual equipment. The indirect costs are estimated as percentages of TIC as shown in Table 6. The expected accuracy of estimate is ±30%, typical of a study estimate [34].

Finally, the operating costs are calculated according to Table 7. Fixed operating costs are calculated as a percentage of TIC while variable operating costs are calculated based on the cost of the consumables.

Once the capital and operating costs are calculated, the minimum ethanol selling price is calculated as the ethanol price which makes the net present value of the project zero with a 10% rate of return. The economic parameters used for the discounted cash flow analysis are shown in Table 8.

Table 5. Data for capital cost calculations of the most important equipment.

Unit	Base purchase cost (MM$)	Reference year	Scale factor (n)	Units	Base Scale	Installation factor	Reference
Indirectly-heated biomass gasifier	27.3	2008	0.70	dry tonne biomass/day	550	1	supplier
OLGA	-	-	-	-	-	-	confidential
Syngas compressor	5.85	2009	0.70	MW_e	5.44	1.32	supplier
LO-CAT	1.0	2002	0.65	lb sulphur/hour	108	2.47	[2]
SMR	41.0	2002	0.60	kmol total reformed/hour	1,277	1	[32]
Amine CO_2 capture system	15.4	2001	0.65	lb CO_2/hour	100,203	2.47	[33]
LPMEOH reactor	5.1	2002	0.60	tonne methanol/hour	18.9	2.10	[23]
Gas turbine and Combustor	19.09	2003	0.70	MW_e	26.3	1	[18]

Scaling equation: $Cost/Cost_{base} = (Scale/Scale_{base})^n$.

The installation factor is 1 if the base cost already includes the indirect costs.

Table 6. Cost factors for estimating direct and indirect costs as a percentage of purchase cost equipment (PEC) and total installed cost (TIC), respectively.

Direct Cost	% PEC
Purchase equipment installation	39
Instrumentation and control	26
Piping	31
Electrical systems	10
Building (including services)	29
Yard improvements	12
Total direct costs	147
Indirect Costs	**% TIC**
Engineering design and procurement	7.9
Contractor Management and control	2.2
Capital spares and other costs	2.0
Operator training	1.0
Start up assistance	1.0
EPC constructor contingency	15.0
Total indirect costs	29.1

Table 7. Data for calculating operating costs.

Fixed operating costs	% TIC
Labor	1.56
Maintenance	1.50
General expenses	3.07
Management and operation services	0.44
Cost of Goods Sold- Marketing, Logistics and others	1.32
Insurance	0.50
Total	8.39
Variable operating costs	
Biomass (USD/dry tonne)	66
SMR catalyst (USD/kg)[a]	10.30
LPMEOH catalyst (USD/L methanol)	0.0044
Hydrocarbonylation catalyst (USD/L ethanol)[b]	0.0044
Lo-Cat Chemical (USD/kg sulfur produced)	0.15
Waste water (USD/m^3)	0.731
Boiler chemicals (USD/tonne)	0.12
Water demineralization (USD/tonne)	0.34
Ash disposal cost (USD/tonne)	29.02

[a] GSHV (standard conditions) =1780 h^{-1}, 25% catalyst replacement per year, catalyst density = 910 kg/m^3.

[b] assumed (no better data available).

Table 8. Economic assumptions for discounted cash flow analysis. Working capital and cost of land are recovered at the end of plant life.

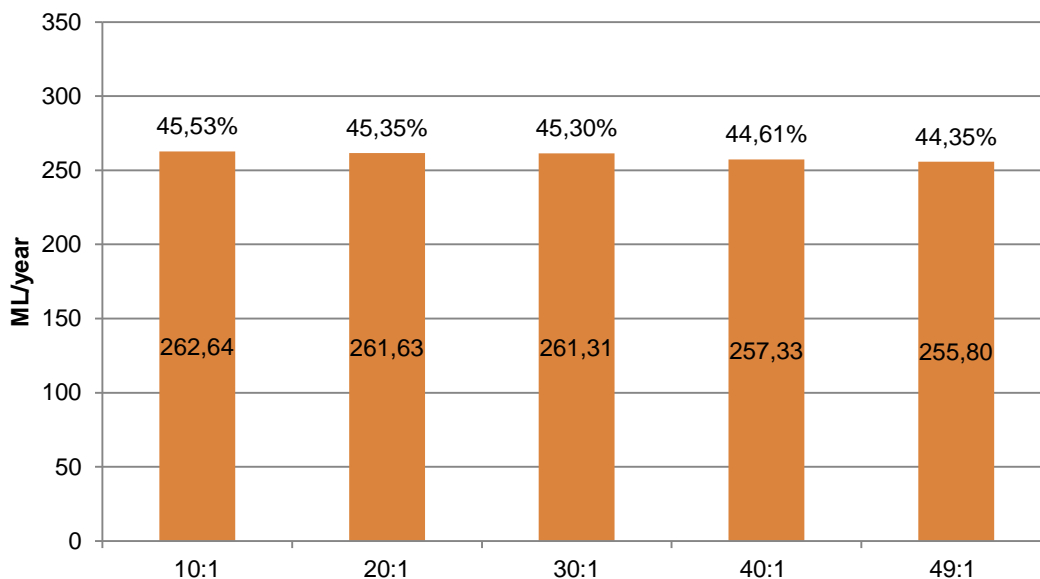| Parameter	Value
Rate of return	10%
Debt/Equity	0/100%
Plant life	20 years
Depreciation (Linear)	10 years
Salvage value	0 M USD
Construction period	1 year
Income tax	30%
Working capital	1-month operating costs
Land	6% TIC

Figure 3. Ethanol production and Biomass to Ethanol efficiency (% HHV) for evaluated cases.

5. Results and Discussion

5.1. Process discussion: material and energy balance results

Figure 3 shows that ethanol production varies from 255.8 for 49:1 case up to 262.6 ML/year for 10:1 case (a variation of only 2.6%), or equivalently, energy efficiency of biomass to ethanol ranges from 44.35 to 45.53 % (HHV basis). The ethanol production is very similar for all cases despite differences in DME conversion and ethanol selectivity for different CO/DME ratios. These results also prove that using a H_2/CO ratio different from 1 in the hydrocarbonylation reactor does not affect global productivity. First, it must be taken into account that the global selectivity to ethanol is theoretically 100%, irrespective of selectivity to ethanol in the hydrocarbonylation reactor, as methanol co-produced in the reactor is recycled to be converted back into DME while methyl acetate is also recycled to be hydrogenated into ethanol. The reason why ethanol productivity decreases with the CO/DME ratio is that the amount of syngas used to satisfy the power demand increases, diminishing the syngas available for ethanol production. The power demands of the plant are shown in Figure 4. As the CO/DME ratio increases the power demands of the plant increase due to larger power consumption in the compressors of the hydrocarbonylation loop and methanol area. Therefore, we can conclude that there is no benefit in achieving large per-pass conversion of DME by operating with large CO/DME ratios, from an energy point of view.

5.2. Economic results

As shown in Figure 5, the minimum ethanol selling price (MESP) increases with the CO/DME ratio from 0.555 to 0.592 USD$_{2010}$/L. Therefore, as previously mentioned, a low CO/DME ratio is economically favored despite of low DME per-pass conversion and selectivity to ethanol. These

results are currently not competitive. The current US market price of corn fuel ethanol is 0.45 USD_{2010}/L [35] and in Europe bioethanol prices are approximately 0.67-0.69 USD_{2010}/L [36].
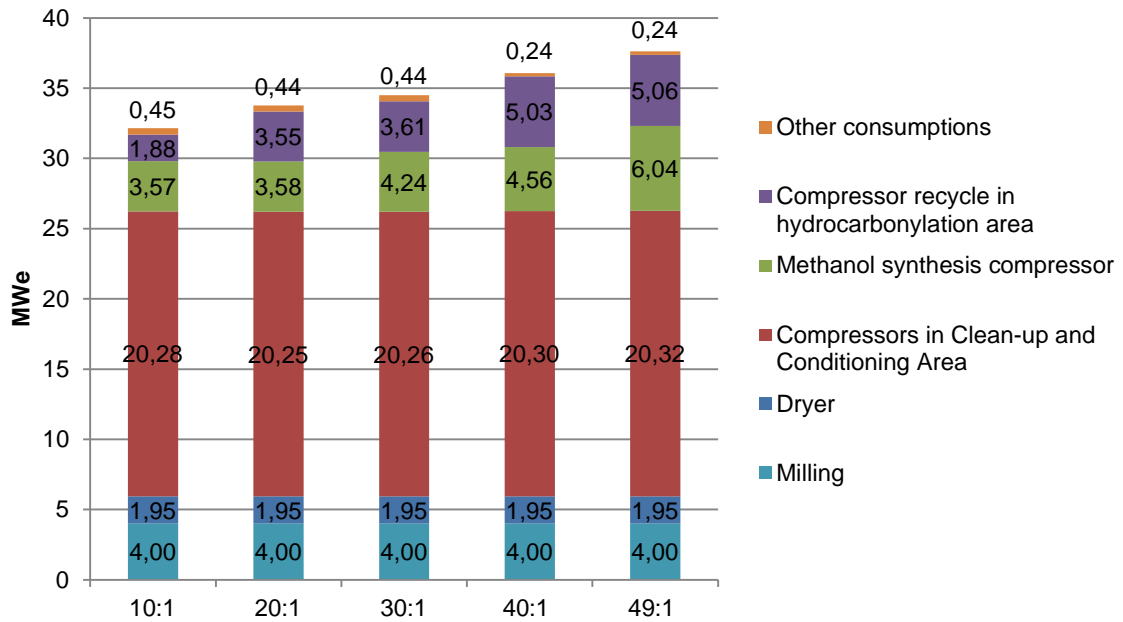

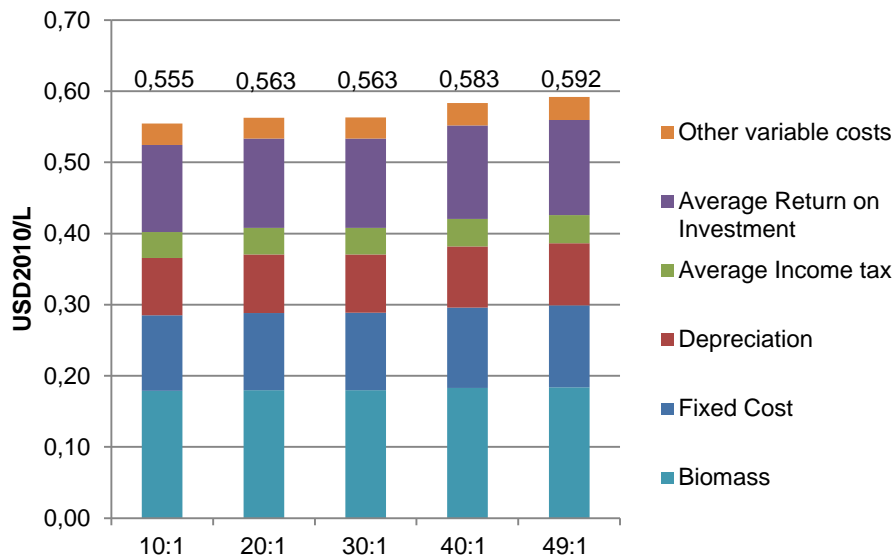**Figure 4.** Electrical power consumption for each CO/DME ratio.

Figure 5. Ethanol Production cost for each case. Other variable costs include all variable costs except biomass costs.

The break-down of MESP in Figure 6 shows that in all cases, the MESP is equally distributed between the operating costs (biomass, fixed costs and other variable costs) and recovery of the investment (depreciation and return on total investment). The biomass cost and fixed costs are the most important operating costs (Figure 6) and each of them equally contributes to the MESP. Catalyst costs only account for about 4-6% of the total operating cost, since this process uses inexpensive commercial catalysts.

Figure 7 shows that fixed capital cost increases from 332.56 to 352.12 M USD$_{2010}$ as CO/DME ratio increases from 10 to 49. Biomass pretreatment and gasification, and gas clean-up and conditioning account for 45-50% of the fixed capital cost. The synthesis area (methanol, DME and hydrocarbonylation) and CO_2 capture system account for 22% of the fixed capital cost. The fixed capital cost increases with CO/DME ratio because of the increase in the cost of the power island, which is a consequence of the larger power demands of the plant.

A sensitivity analysis of ethanol price (MESP) to biomass price (±60%, i.e. from 30 to 100 USD/dry tonne) and total investment cost (±30%) has been carried out as there is an important uncertainty in both costs. Ethanol price would vary ±0.1 USD/L (Figure 8), irrespective of the CO/DME case. The same variation of ethanol price occurs for a ±30% change in TIC (Figure 9), indicating that the ethanol price is more sensitive to TIC than to biomass price. Despite of the uncertainty, the MESP is close to ethanol market prices in Europe.
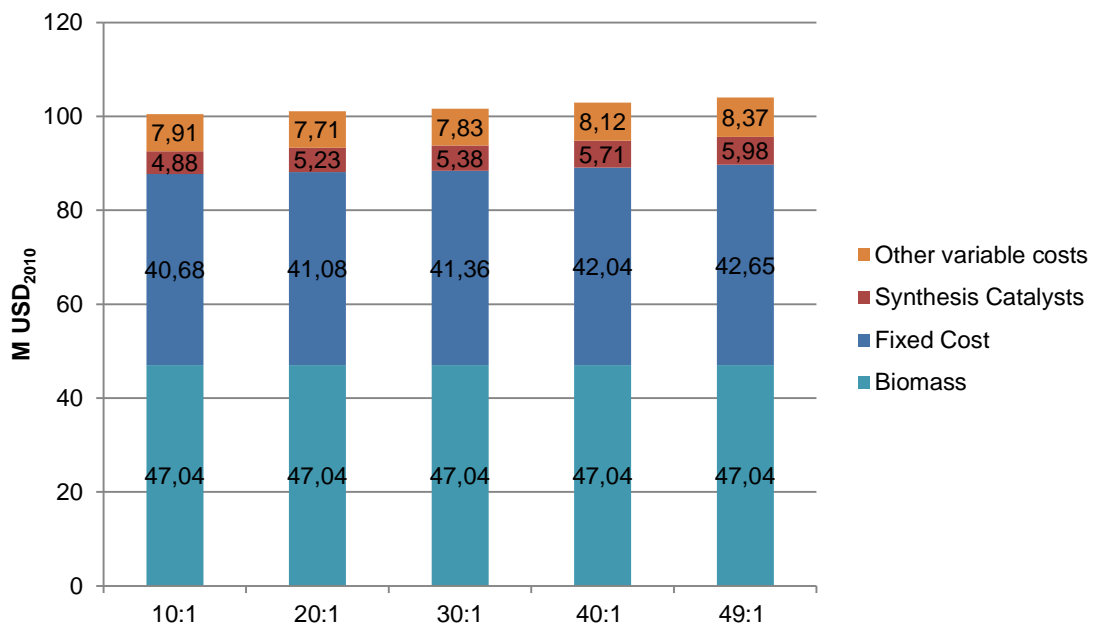
Figure 6. Break-down of operating costs for each case. Other variable costs include all variable costs except biomass and synthesis catalyst costs.
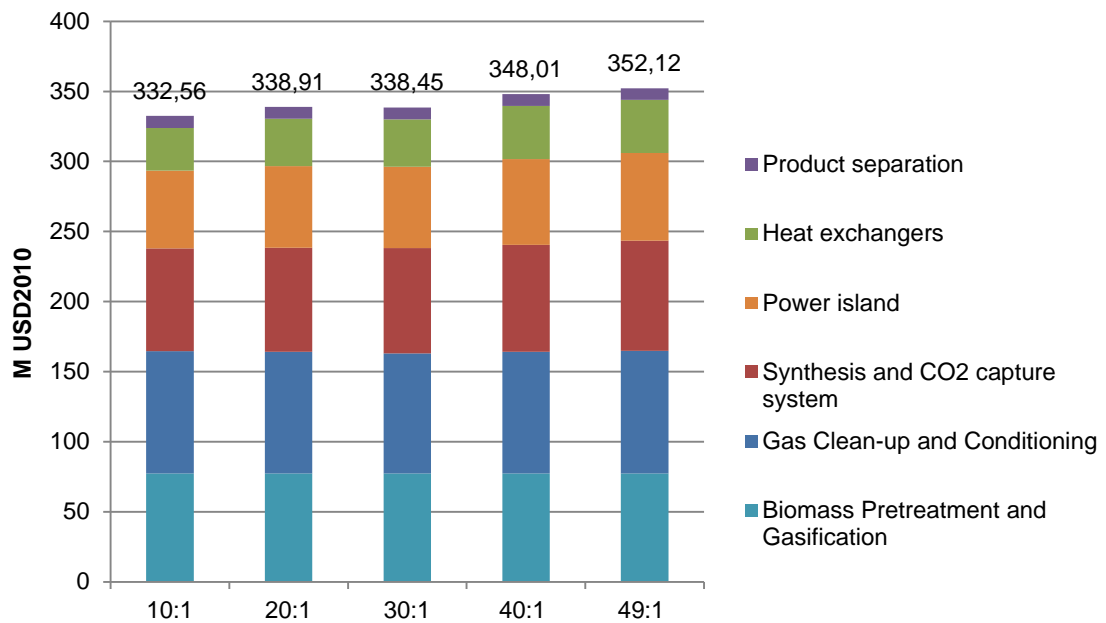
Figure 7. Break-down of fixed capital costs for each case. Note: land cost is not included.
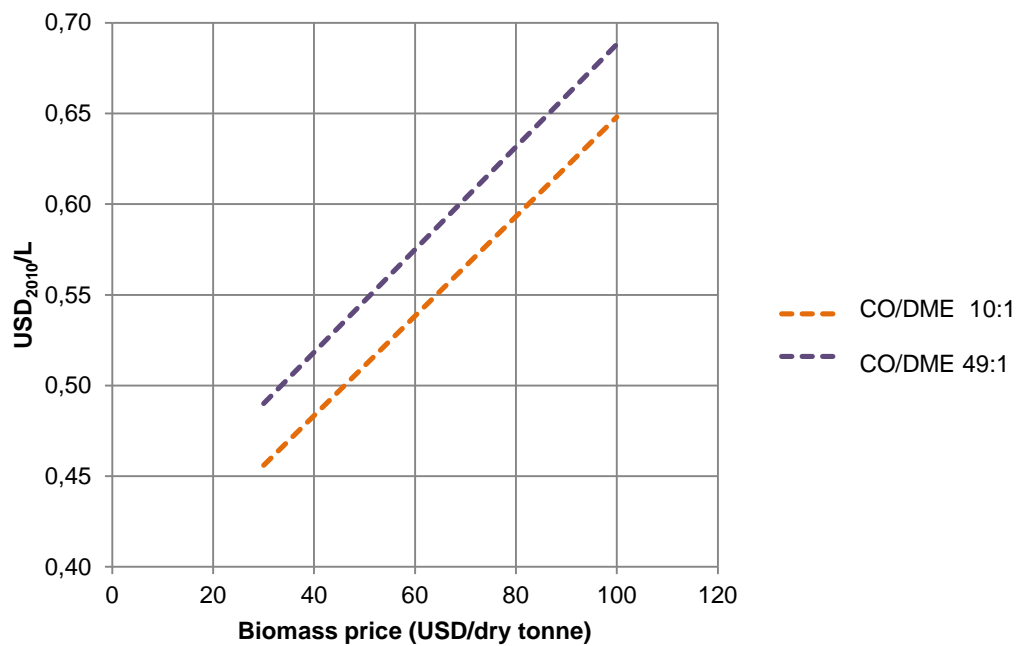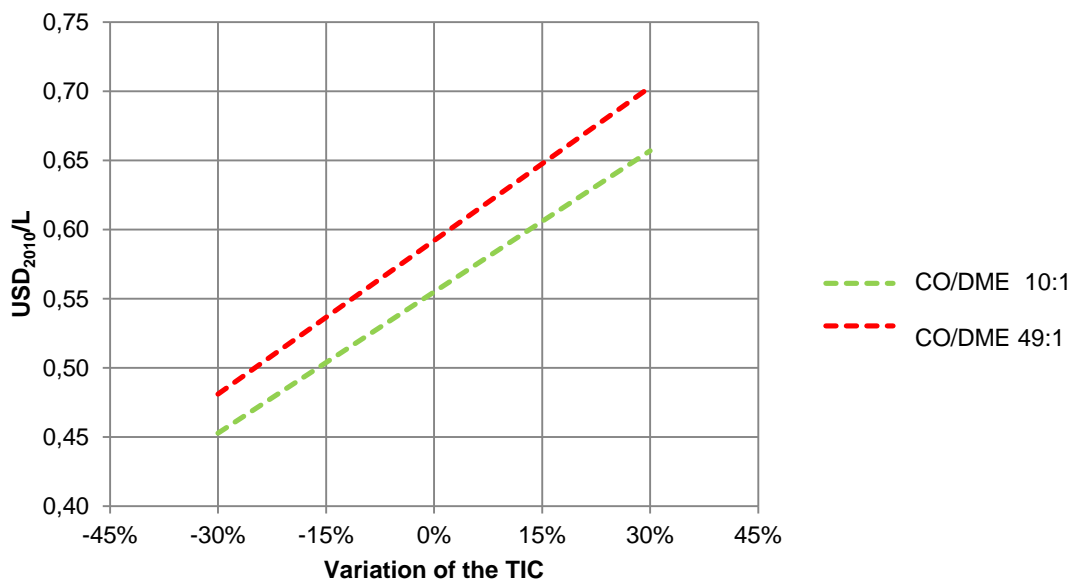

Figure 8. Sensibility analysis of MESP to biomass price for the largest and lowest CO/DME cases. Biomass price for base case is 66 USD/dry tonne.

Figure 9. Sensibility analysis of MESP to a ±30% uncertainty in investment costs for the largest and lowest CO/DME cases.

5.3. Comparison with other bioethanol routes

Table 9 compares the result of this work with other studies on thermochemical [2] and biochemical [37] processes to produce ethanol from lignocellulosic biomass. In these studies, the processes are designed to be energy self-sufficient and the economic assumptions are similar to this work (10% rate of return, 20 year plant life). MESP for the DME hydrocarbonylation process is lower than "state of the art" 2nd generation biochemical processes. NREL (National Renewable Energy Laboratory) assessments of a targeted (i.e. non-existent) synthesis catalyst and tar reformer catalyst for the thermochemical direct route show lower production costs than the proposed indirect route. The main reason for this is the great improvement in the performance of direct synthesis catalysts assumed by NREL and also their much lower biomass price and equipment costs. For instance, if feedstock price assumed by NREL were used in our assessment, the MESP for the hydrocarbonylation route would decrease from 0.555 to 0.515 USD$_{2010}$/L (7.2% reduction). For this reason, a direct comparison with NREL's works is unfair as two different scenarios (present and future) and biomass price are considered.

6. Conclusions

This technoeconomic assessment shows that the production cost of ethanol via the DME hydrocarbonylation route is lower than that reported in the literature for the production of lignocellulosic ethanol via biochemical pathway [37]. Thus, ethanol from the DME route looks promising. This study has raised some important issues with regard to catalyst performance which should be investigated in order to optimize the design of the process such as performance of the hydrocarbonylation catalyst at different H_2/CO ratios.

As compared with the "state of the art" biochemical synthesis route, the ethanol production cost via the DME hydrocarbonylation route is lower because its larger energy efficiency and selectivity to ethanol outweigh its complex configuration. Hence, the thermochemical ethanol production via the DME hydrocarbonylation route could be cost-competitive in the near future.

Table 9. Comparative results from this study with other comparable thermo and biochemical processes. All data are up-to-date and refer to 2010.

	This work	NREL (CFB+ targeted MoS$_2$ synthesis catalyst) [2]	2nd Generation biochemical [37]
Feedstock price (USD/dry tonne)	87[a]	51	87
Plant size (dry tonne/day)[b]	2140	2000	2000
Ethanol production (ML/year)[c]	263	234	202
Export of electricity (MWe)[d]	0	0	25.8
Total Capital Investment (M USD)[e]	434.1	252.4	395
Extra revenues (M USD/year)[f]	0	42	12.3
Net operating costs (M USD/year)[g]	97.1	81.9	124.5
MESP (USD/L)	0.613	0.353	0.95
Biomass to ethanol efficiency (%HHV)	45.53	47.4[h]	-

[a] For comparison proposes, the 10:1 case has been updated with a 87 USD$_{2010}$/dry tonne price.

[b] Biomass feedstock for biochemical processing is corn stover (25% moisture); other: poplar chips (30% moisture).

[c] 8000 operating hours per year for DME process; other: 8406.

[d] Sold to grid, 5.7 cent/kWh credits for electricity.

[e] Including working capital.

[f] Revenues from electricity or co-products.

[g] Fixed and variable operating costs less revenues from electricity or co-products.

[h.] Efficiency to total alcohols

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