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Chemical storage of wind energy by renewable methanol production: Feasibility analysis using a multi-criteria decision matrix

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Abstract

This study is for the technoeconomic analysis of an integral facility consisting of wind energy-based electrolytic hydrogen production, bioethanol-based carbon dioxide capture and compression, and direct methanol synthesis. ASPEN Plus was used to simulate the facility producing 97.01 mt (metric tons) methanol/day using 138.37 mt CO₂/day and 18.56 mt H₂/day. A discounted cash flow diagram for the integral facility is used for the economic analysis at various hydrogen production costs and methanol selling prices. The feasibility analysis is based on a multi-criteria decision matrix consisting of economic and sustainability indicators comparing renewable and non-renewable methanol productions. The overall energy efficiency for the renewable methanol is around 58%. Fixation of carbon reduces the CO₂ equivalent emission by around –1.05 CO₂e/kg methanol. The electrolytic hydrogen production cost is the largest contributor to the economics of the integral facility. The feasibility analysis based on multi-criteria shows that renewable methanol production may be feasible.

Keywords: Electrolytic hydrogen, CO₂ fixation, Methanol production, Technoeconomic analysis, Sustainability metrics, Multi-criteria decision matrix

1. Introduction

The generation of renewable electricity suffers from intermittent and fluctuating character and necessitates the storage. Wind energy-based electrolytic hydrogen may serve as a chemical storage for renewable electricity [1–5]. Hydrogen is a clean fuel, its burning causes no harmful emissions, and it has a gravimetric heating value three times higher than typical hydrocarbon fuels [1, 2]. On the other hand, the cost to produce, store, compress, and transport hydrogen is still high [6–9]. The synthesis of methanol from CO₂ and electrolytic hydrogen can also store this electrical energy. Methanol synthesis can fix the CO₂ when its used as feedstock for producing various chemicals, such as formaldehyde, acetic acid, methyl methacrylate and their derivatives, and also be used as transportation fuel and hence recycles CO₂ [10–15].

Rihko-Struckmann et al. [16] carried out an energetic evaluation in order to assess the overall efficiency of methanol and hydrogen-based storage systems for renewable electric energy; the efficiency of the system using hydrogen is higher compared with that of using methanol as storage medium; however, storage and handling of methanol as chemical storage is favorable when compared with H₂. Tremel et al. [5] investigated the economics of producing five fuels from electrolytic hydrogen. Of these five fuels, methanol performed the best overall, receiving high marks in terms of

economics and technology. CO₂ hydrogenation has also been simulated by Van-Dal and Bouallu [17, 18] showing that the production of methanol can fix large quantities of CO₂. The production of hydrogen using carbon free electricity was highly stressed in these papers, as if as little as 20% of the electrolysis energy is the result of a coal fired plant the CO₂ abatement becomes null. As well Pontzen et al. [19] studied methanol production from CO₂ and H₂, showing that CO₂ fixation can be achieved using a commercial Cu/ZnO/Al₂O₃ catalyst and is possible on a large scale. However, a main concern listed is the associated costs and energy of producing and purifying CO₂ and H₂ again using carbon neutral sources. Mignard et al. [20] conducted an economic feasibility study of a methanol production using CO₂ and renewable electricity in 2003 by using CO₂ from flue gas.

This study is for a comprehensive feasibility analysis of methanol production using wind-based electrolytic hydrogen and CO₂ captured from an ethanol plant. Electricity from wind power is used since its levelized cost is comparable with hydropower, and around 38% lower than that of solar photovoltaic as seen in Table A1 [1, 2]. Costs and energy requirements are calculated for wind-based H₂ and ethanol-based CO₂ production, compression, and storage. The economic feasibility of methanol plant using these inputs is investigated with varying production costs of electrolytic hydrogen and methanol selling prices. A multi-criteria decision

matrix has been created to include sustainability metrics, along with economic factors, in a comparative feasibility analysis of the renewable methanol option with conventional fossil fuel-based methanol synthesis.

2. Sustainability

The following sustainability metrics can be applied for chemical processes [21, 22]:

- Material intensity (nonrenewable resources of raw materials, solvents/unit mass of products)
- Energy intensity (nonrenewable energy/unit mass of products)
- Potential environmental impact (pollutants and emissions/unit mass of products)
- Potential chemical risk (toxic emissions/unit mass of products)

This study uses the sustainability metrics of 'material intensity', 'energy intensity' and 'potential environmental impact' as emissions of CO₂e by using the 'Carbon Tracking' and the 'Global Warming Potential' options [21, 22]. The carbon tracking is based on the emission factor data source of US-EPA-Rule-E9-5711, while the global warming potential is based on the US-EPA's (CO₂E-US) with the fuel source of natural gas and a predetermined cost for CO₂e fee/tax of \$2/mt CO₂e [23–25].

3. Hydrogen production

3.1. Hydrogen production from syngas

Currently, 96% of H₂ is produced directly from steam reforming of natural gas, coal gasification, and partial oxidation of hydrocarbons such as biomass [10, 26, 27]. Figures 1 and 2 show some commercial processes for H₂ production from syngas feedstock with carbon capture and storage. These processes are complex, sensitive to the feedstock quality, and require large investments for larger units. The generated carbon monoxide can also be used in the water-gas shift reaction to yield more hydrogen. In these processes, however, at least 20% of the energy of the fossil fuel is lost as waste heat [10].

Energy efficiency for biomass-based H₂ production is around 60% and likely become competitive in the future [10, 27]. Most modern plants purify the crude H₂ to 99.99-wt% by removing methane, CO₂, N₂, and CO using multi-bed pressure swing adsorption [10, 28–30].

Current production of H₂ from natural gas and coal accounts for 48% and 18% of the total production, respectively. The emissions of CO₂ vary between 7.33 kg CO₂/kg H₂ and 29.33 kg CO₂/kg H₂ using conventional fuels at about 75% energy efficiency. CO₂ emission (beside SO_x and NO_x) associated with producing H₂ from coal is about two to three times higher than that of the H₂ produced from natural gas [2, 10].

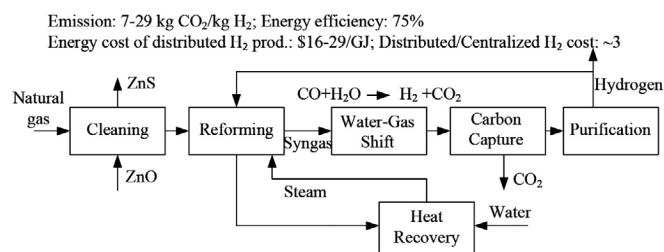


Fig. 1. Hydrogen production by steam reforming of natural gas [10, 26].

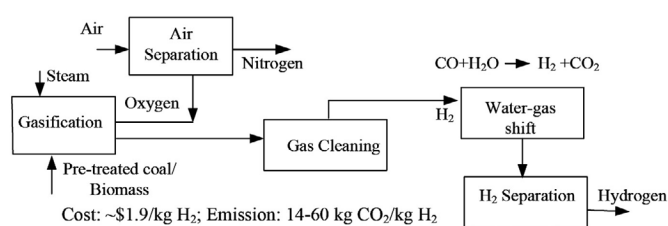


Fig. 2. Hydrogen production by gasification of coal [10, 28–30].

3.2. Wind-based electrolytic hydrogen production

Renewable hydrogen comes from the electrolysis of water using hydropower, wind power, and solar photovoltaic power. Fig. 3 shows the schematic of wind energy-based hydrogen production. Alkaline electrolysis technologies are the most mature commercial systems. The system includes the transformer, thyristor, electrolyzer unit, feed water demineralizer, hydrogen scrubber, gas holder, two compressor units to 30 bar, deoxidizer, and twin tower dryer [7, 8]. These electrolyzers have the energy efficiencies of 57%–75%. The typical current density is 100–300 mA/cm² [4–9].

For producing one kg H₂, approximately 26.7 kg water is necessary; electrolysis uses approximately 45% of this water while manufacturing the wind turbines and the hydrogen storage consume around 38% and 17% of the water, respectively. The total greenhouse gas emission is around 0.97 kg CO₂e/kg H₂, which is distributed approximately as 0.757 kg CO₂e/kg H₂ (78%) for the wind turbine production and operation (because of steel and concrete used in its construction), 0.043 kg CO₂e/kg H₂ (4.4%) for the electrolyzer construction and operation, and 0.17 kg CO₂e/kg H₂ (17.6%) for the hydrogen compression and storage (mainly due to the production of steel used in the storage tanks) [6, 7]. The hydrogen production cost is highly dependent on the electricity price, which may be around 75% of the final cost. Therefore electrolysis plants take advantage of low electricity prices at off-peak hours [7, 9].

3.3. Hydrogen economy

Mueller-Langer et al. [27] evaluated hydrogen production processes based on natural gas steam reforming, coal and biomass gasification, and water electrolysis. The H₂ production cost is around \$65/GJ using wind electricity, \$30/GJ using nuclear power, and \$600/GJ using photovoltaic electricity based on 2007 U.S.\$. Large-scale processes, using natural gas and coal, are the most economical processes while biomass gasification still needs technological improvements before becoming competitive [10, 27].

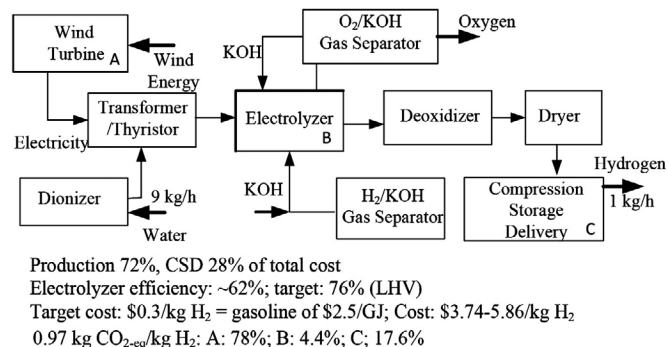


Fig. 3. Schematic for alkaline electrolysis of water for hydrogen production with compression, storage and delivery [6–10, 26–30].

The cost of electrolytic hydrogen depends on the cost of electricity as well as the capital cost of the electrolyzer systems and their operating efficiency. The current capital equipment cost for advanced electrolysis is between \$600/kW and \$700/kW. This cost needs to be reduced to \$200/kW to achieve \$2.75/GGE (untaxed gasoline gallon equivalent) by 2015 [9, 31, 32]. The primary research challenge is to reduce the capital and operating costs of electrolysis systems; as the wind turbines are not designed to produce hydrogen from electrolyzers, which typically operate using constant direct current supply. Declining of coal-fired and nuclear electricity generation capacity may lead to gain in electricity generation by natural gas and renewables. Capital cost of electrolyzer increases considerably as the wind farm availability and electrolyzer capacity decrease [9, 26, 30, 31].

The unit cost estimates of wind power-based electrolytic H₂ are also limited geographically and range from \$3.74/kg H₂ to \$5.86/kg H₂. With the combined effects of tax credits of \$0.02/kWh they become \$2.76/kg H₂ to \$4.79/kg H₂ [9]. The capacities of H₂ productions range from 1000 to 50,000 kg H₂/day [2–5]. Other factors such as large-scale storage, compression, pipeline transport, and dispensing economics need separate analyses. However, using the off-peak power could increase plant load factor and improve the economics [32–34].

A standard commercial electrolyzer unit, like the Norsk Hydro atmospheric type electrolyzer unit, produces 0.09 kg H₂ and 0.71 kg O₂ per kg of H₂O fed [7, 8]. Typical output concentrations are 99.9–99.9998% for H₂ and 99.2–99.9993% for O₂ [4, 6]. To help subsidize the cost of hydrogen production the O₂ produced could be sold to a nearby chemical processing plant or oxy-fuel combustion power plant [17, 20]. Sale to an oxy-fuel power plant would also aid in carbon capture associated with conventional fossil fuel-based energy production. Without selling the O₂ however, the leveraged cost is \$6.63/kg H₂ (2007\$) and the purchased electrolyzer system cost: \$489/kW (2014\$). Economic analysis shows that final production cost is around \$4.97/kg H₂, which is much higher compared with the cost of \$1.91/kg H₂ from coal gasification [7, 8].

Electricity cost is typically 70–80% of the total cost of H₂ production. Table 1 shows the typical energy usage, including product compression, by the Norsk electrolyzer [7, 8]. The minimum power conversion system would require rectification of the variable alternating current output from the wind turbines to direct current output for the electrolyzer cells. Current state-of-the-art electrolysis conversion efficiency is 67% based on LHV (lower heating value), only slightly less than the DOE (Department of Energy) 2014 target of 69%. DOE's 2014 targets for electrolyzer capital costs are expected to fall to \$400/kW for distributed and \$350/kW for central production facilities. DOE's production target is \$2/kg H₂ [31, 32] while the IEA (International Energy Agency's) cost target for hydrogen is around \$0.30/kg H₂, which will correspond to an energy price for gasoline of \$2.5/kg H₂ [33, 35].

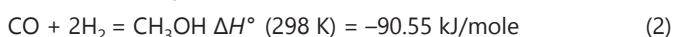
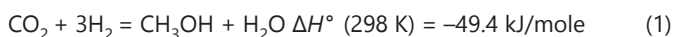
4. Carbon dioxide capture and compression

Some of the available sources for CO₂ are fermentation processes such as ethanol production plants, fossil fuel-based power stations, ammonia, and cement plants [36, 37]. Table 2 shows the equipment and operating costs to capture and liquefy 68 mt CO₂/day and 272

mt CO₂/day (the maximum capture rate for a typical 40 million gal/year ethanol plant). The estimated costs are for food grade CO₂ (99.98% minimum and <0.4 ppmv of sulfur) and also for less purified CO₂ suitable for enhanced oil recovery or sequestration [36].

5. Methanol synthesis

Methanol synthesis needs carbon-rich feedstock (natural gas, coal or biomass), hydrogen, and a catalyst, mainly Cu/ZnO/Al₂O₃ [39–45]. Methanol is produced almost exclusively by the ICI, the Lurgi, and the Mitsubishi processes. These processes differ mainly in their reactor designs and the way in which the produced heat is removed from the reactor. To improve their catalytic performance, the CuO/ZnO catalysts have been modified with various metals, such as chromium, zirconium, vanadium, cerium, titanium, and palladium [42, 46, 47]. Table 3 shows some of the experimental reactor operating temperatures and pressures with the catalyst Cu/ZnO/Al₂O₃. During the synthesis these following reactions occur [46, 47].



Only two of these reactions are linearly independent and their reaction rate equations can describe the kinetics of the all reactions.

5.1. Methanol from fossil fuels

Fig. 4 shows the main blocks of natural gas-based methanol production. Three fundamental steps are: (i) natural gas reforming to produce syngas with an optimal ratio of [(H₂ – CO₂)/(CO + CO₂)] = 2, (ii) conversion of syngas into crude methanol, and (iii) distillation of crude methanol. Methanol synthesis from natural gas emits around 1.6 kg CO₂/kg methanol. Commercial process of methanol production from natural gas is the most efficient process with a typical energy efficiency of 75% (Table 4) [10]. Specific energy consumption for natural gas-based methanol is around 8.0 GJ/mt methanol [35].

5.2. Methanol economy

The coal-based syngas process has the highest emission of GHG (greenhouse gasses), which is around 2.8–3.8 kg CO₂/kg methanol. Typical energy efficiency for the coal-based methanol is in the range of 48%–61% as shown in Table 4 [10, 35]. Technical and economic analyses of methanol production from biomass-based syngas show that overall energy efficiency is around 55% based on HHV (higher heating value). The level of emission is around 0.2 kg CO₂/kg methanol, which is mainly from biomass growing, harvesting, and transportation. Methanol from biomass or flue gas CO₂ is at least 2–3 times more expensive than the fossil-fuel based methanol (Table 4) [10, 47, 53]. Methanol synthesis from water, renewable electricity, and carbon may lead to chemical storage of renewable energy, carbon recycle, fixation of carbon in chemical feedstock, as well as extended market potential for electrolysis.

Table 1. Energy usage for the Norsk Hydro bipolar alkaline electrolyzer [7,8].

	System energy required kWh/kg H ₂	Hydrogen production at highest rate kg/h (kg/year)	Electrolyzer energy required at maximum rate kW
High pressure ~16 bar	53.4	5.4 (47,000)	290
Atmospheric	53.4	43.4 (380,000)	2300

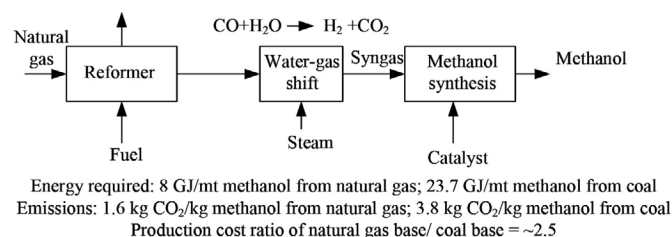
Table 2. Estimated cost of CO₂ recovery options from ethanol plant (\$ 2014) [36].

Cost	68 mt CO ₂ /day Beverage grade	272 mt CO ₂ /day Beverage grade	272 mt CO ₂ /day Non-beverage grade
Capital cost, \$	2,841,061	6,479,415	5,277,859
Capital cost, \$/mt CO ₂	41,780.32	23,821.40	19,403.92
Electricity, ^a \$/mt CO ₂	22.57	21.79	21.89

a. Electricity cost: \$0.10/kWh; Cost (2014) = Cost (2006) [CEPCI(2014)/CEPCI(2006)]; CEPCI(2006) = 499.6 and CEPCI(2014) = 576.1 [38], CEPCI: Chemical Engineering Plant Cost Index.

Table 3. Experimental conditions of methanol synthesis with the catalyst Cu/ZnO/Al₂O₃.

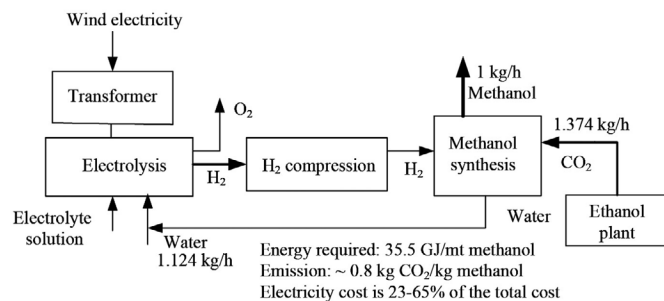
Reactions	T, °C	P, bar	Ref.
Based on all three reactions (1–3)	250	50	[46]
Based on all three reactions (1–3)	200–244	15–50	[48]
Based on reaction (1) and (2)	215–270	50	[49]
Based on all three reactions (1–3)	240	5–70	[50]
Based on reaction (1) and (3)	180–280	51	[51]
Based on reaction (1) and (3)	250	30	[52]

**Fig. 4.** Main blocks in Lurgi's methanol production from natural gas [10, 35].

Currently the cost for hydrogen from electrolysis is roughly twice of that from natural gas steam reforming; however, a significant GHG reduction may be possible [35]. Clausen et al. [53] used electrolytic H₂ in methanol production using the post combustion captured CO₂. The alkaline electrolyzer is operated at 90 °C and atmospheric pressure with an electricity consumption of 4.3 kWh/Nm³ H₂ corresponding to an efficiency of 70% (LHV). With underground storage for hydrogen and oxygen and the electricity price during the off-peak hours of operation, the costs are estimated as \$217/mt methanol (2010 \$) (with energy price of \$15.0/GJ, and carbon capture price of \$20.0/mt CO₂). The electricity cost accounts around 23%–65% of the methanol production cost because of high stoichiometric hydrogen demand in the synthesis [49,51,54]. With coal as carbon source, 23.7 GJ/mt methanol and with CO₂ as carbon source 35.5 GJ/mt methanol are required [10, 35].

5.3. Methanol synthesis from CO₂ and H₂

Converting CO₂ into chemicals is thermodynamically challenging, and inherently carries costs for the energy and hydrogen

**Fig. 5.** Schematic of methanol production using renewable hydrogen and CO₂ [10, 35, 46].

supply [35]. The conversions of reactions (1) to (3) with catalyst of Cu/ZnO/Al₂O₃ are limited by the chemical equilibrium of the system. The temperature rise must be minimized in order to operate at good equilibrium values. However, selectivity for methanol is high with a value of 99.7% at 5 MPa and 523 K with a H₂/CO₂ ratio of 2.82 [46]. The energy efficiency for the concentrated CO₂ and hydrogen based methanol is around 46% [10,35,46]. Fig. 5 shows a schematic of wind electricity-based hydrogenation of CO₂ to methanol.

We designed and simulated a methanol plant using ASPEN Plus software. Wind-based electrolytic H₂ and CO₂ supplied from an ethanol plant are used in the synthesis of methanol. The plant uses 18.6 mt H₂/day and 138.4 mt CO₂/day, and produces 97.0 mt methanol/day at 99.5 wt% together with 54.6 mt/day of 99.5 wt% H₂O waste water. Fig. 6 presents the process flow diagram for the methanol plant using CO₂ and H₂. We chose to use the RK-SOAVE property method for estimating the properties of the mixture with gaseous compounds at high temperature and pressure, and the NRTL-RK for the methanol column to better represent the vapor–liquid equilibrium between methanol and water. CO₂, H₂ and CO were defined as Henry's components with this property method. The feedstock is at the conditions associated with typical storage, with H₂ at 25 °C and 33 bar and CO₂ at –25.6 °C and 16.422 bar (liquid phase) [6]. The ratio of H₂ to CO₂ is held at of 2.1:1 to promote methanol synthesis. In the feed preparation block, the renewable H₂ and CO₂ are compressed to 50 bar in a multi-stage compressor and pump, respectively, and mixed with the recycle stream S12 in mixer M101. Stream S1 is preheated in HX101 and E101 before being fed into the plug-flow reactor R101 where the methanol synthesis takes place

Table 4. Costs and emissions^b from various methanol productions process [10, 35].

Process	Production cost \$/mt methanol ^a	Emissions kg CO ₂ /kg methanol	Energy efficiency %
Natural gas based syngas	165	0.5–1.6	75
Coal based syngas	418	2.8–3.8	48–61
Biomass based syngas	700	0.2	51
CO ₂ from flue gas	942	0.8	46

a. The cost data [10] for 2005 has been updated using: Costnew = Costold [CEPCI(2014)/CEPCI(2005)]CEPCI (2014) = 576.1 and CEPCI (2005) = 468 [38].

b. This emissions account for methanol production process as well as the emissions occurring with the utilization of methanol.

Table 5. Column specifications and results for column T101.

Column specification/results	Value
Stages	20
Feed stage	15
Height (m)	20
Diameter (m)	1.16
Reflux ratio (molar)	0.959
B:F ^a (molar)	0.498
Condenser temp (°C)	55

a. B:F Bottom flow to feed ratio.

steam produced (TFR101 OUT) to preheat the reactor input from inlet conditions (−14 °C) to reactor operating conditions (235 °C). The reactor effluent would then be used to preheat the distillation column feed to the feed stage temperature. Both of these designs of steam use and heat integration represent energy efficient methods of methanol production from renewable inputs.

The separation section uses an optimized process using one column for methanol distillation. While gas removal and heat integration could be accomplished by using multiple columns [56] the additional capital and operating costs associated with multiple columns could make the process less economically feasible. This work represents a practical example of methanol production using kinetics based on experimental data using a commercially available catalyst [49]. However, future work to improve the process could be conducted including; heat integration between the H₂ and CO₂ production plants and in the methanol process itself, further column optimization using ASPEN Plus column targeting tools, optimization of recycle flash drums to minimize the duty of C102 while increasing CO₂ recycle and scale up considerations (Lurgi's two reactor concept) for the production of larger quantities of methanol [55, 56].

6. Results and discussions

6.1. Sustainability analysis

The integral methanol production facility consists of an electrolytic hydrogen production unit, CO₂ capture and storage unit, and the methanol production unit as shown in Fig. 7. Table 6 shows the sustainability indicators of the integral methanol plant. The facility requires 18.56 mt H₂/day and 138.37mt CO₂/day in total and produces 97.0 mt methanol/day and 148.39 mt O₂/day. The total emissions of CO₂ from are 18.01 mt CO₂/day for the H₂ production

and 6.10 mt CO₂/day for the CO₂ capture and storage. The methanol production plant reduces emissions by −118.41 mt CO₂/day if the steam produces electricity or by −126.38 mt CO₂/day if the steam is used as process heat. Table 6 shows the main results of the material and energy usages, as well as the CO₂ emissions for the integral facility. The energy costs are estimated by the unit cost of utilities listed in Table A2. The reductions in the net carbon fee range between −\$9.87 and −\$10.53 for the methanol facility depending on how the steam is utilized. This is based on a set value of \$2/mt CO₂e. As Table 6 shows, the values of total duty and cost are the highest for the hydrogen production unit used in the methanol production.

Fig. 8 presents an approximate energy balance with the energy required at the electrolyzer, for carbon capture and storage, and total duty required in methanol production versus energy content in methanol as fuel combusted fully. The energy efficiency for the integral facility for both steam utilization routes is around 57.6%. This is in line with the results shown in Mignard et al. [20] who showed efficiencies ranging from 51 to 58%. A comparison to the values in Table 4 shows that the energy efficiency of this process is comparative with coal and biomass based syngas processes [10, 35].

Table 7 presents the sustainability metrics for the integral methanol plant in which the indicators are normalized with respect to the amount of methanol produced. The material intensity metrics show that the methanol facility requires 1.43 mt CO₂/mt methanol. The energy intensity metrics favors when steam is used to produce electricity, with the net utility cost around \$824.09/mt methanol. The environmental impact metrics show that the integral methanol facility with heat utilization of steam reduces emission by around −1.05 kg CO₂/kg methanol when utilizing it as a chemical feedstock for CO₂ fixation (e.g. formaldehyde, acetic acid, methyl methacrylate, etc.) and recycles 0.32 kg CO₂/kg methanol after its complete combustion when used as a fuel/fuel additive, as seen in Fig. 7.

6.2. Economic analysis

The economic analysis of the integral methanol plant is based on the DCFD (discounted cash flow diagrams) prepared for ten-years of operation using the current technology and economic data. An example calculation of a DCFD is shown in the Appendix. Based on the equipment list from the process flow diagram (Fig. 6), bare module costs are estimated and used as *FCI* (fixed capital investments). Chemical Engineering Plant Cost Index (*CEPCI*-2014) (=576.1) [38] is used to estimate and update the costs and capacity to the present date by

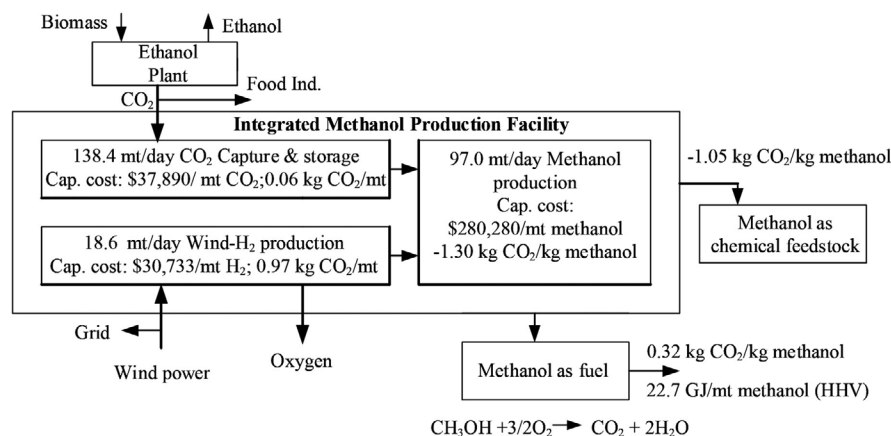
**Fig. 7.** Some economic and sustainability indicators in the integral methanol production facility.

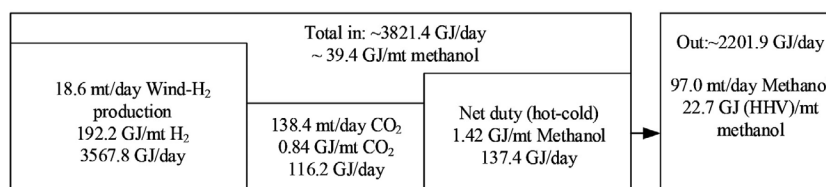
Table 6. Sustainability indicators for the integral methanol plant.^a

Material indicators	Integral methanol production			
	MeOH Prod. ^b	MeOH Prod. ^c	H ₂ Prod.	CO ₂ C&S
CO ₂ /CO ₂ production, mt/day				138.37
H ₂ production, mt/day			18.56	
Methanol production, mt/day	97.01	97.01		
Oxygen production, mt/day			148.39	
Energy intensity indicators				
Total heating/electricity duty, MW	2.38	1.14	41.34	1.26
Total cooling duty, MW	5.79	5.39	0.12	0.06
Net duty (heating – cooling), MW	–3.42	–4.25	41.22	1.20
Total heating cost, \$/h	24.60	31.05	3204.11	97.81
Total cooling cost, \$/h	4.42	4.12	0.09	0.04
Total cost (heating + cooling), \$/h	29.02	35.17	3204.20	97.85
Environmental impact indicators				
Net stream CO ₂ e, mt/day	–133.66	–133.66	0.00	0.00
Utility CO ₂ e, mt/day	15.25	7.28	18.01	6.10
Total CO ₂ e, mt/day	–118.41	–126.38	18.01	6.10
Net carbon fee, \$/h	–9.87	–10.53	1.50	0.51

a. US-EPA-Rule E9-5711; natural gas; carbon fee: \$2/mt.

b. Methanol production producing steam.

c. Methanol production utilizing steam as heat.

**Fig. 8.** Overall energy balance for the integral methanol production facility.

$$Cost_{new} = Cost_{old} \frac{CEPCI_{old}}{CEPCI_{new}} \left(\frac{Capacity_{new}}{Capacity_{old}} \right)^x \quad (7)$$

where x is the factor, which is usually assumed to be 0.6. Working capital is 20% of the FCI . Depreciation method is the MACRS (Maximum Accelerated Cost Recovery System) with a 7-year recovery period [57]. After estimating the revenue and the cost of production, DCFD is prepared to estimate the three economic feasibility criteria that are NPV (Net Present Value), PBP (Payback Period), and ROR (Rate of Return). In addition, the EC (economic constraint) and the unit PC (product cost) are also estimated by

$$EC = \frac{\text{Average Discounted Annual Cost of Production}}{\text{Average Discounted Annual Revenue}} \quad (8)$$

$$PC = \frac{\text{Average Discounted Annual Cost of Production}}{\text{Capacity of the Plant}} \quad (9)$$

Table 7. Sustainability metrics for the integral methanol plant, with steam production (a) and with steam utilization (b).

Material metrics	(a)	(b)
CO ₂ used/Unit product	1.43	1.43
H ₂ used/Unit product	0.19	0.19
Energy intensity metrics		
Net duty/unit product, MWh/mt	0.40	0.39
Net cost/Unit product, \$/mt	824.09	825.61
Environmental impact metrics		
Total CO ₂ e/Unit product	–0.97	–1.05
Net carbon fee/Unit product, \$/mt	–1.94	–2.11

* US-EPA-Rule E9-5711; natural gas; carbon fee: \$2/mt [25].

The PC takes into account the O&M (operating and maintenance) costs. An operation with $EC < 1$ shows a more feasible operation with the opportunity to accommodate other costs and improve the cash flows toward more positive NPV . The calculations of average discounted annual cost of production, average discounted annual revenue, and capacity of the plant are given in the appendix equations; A1, A2, and A3, respectively.

At the current capacities, the estimated approximate values of the $FCIs$ are \$5.87 million for the wind-based electrolytic H₂ production unit, \$4.52 million for the CO₂ production unit, and \$28.13 million for the methanol production unit. The H₂ production includes the compression, storage, and dispensing from a centralized production facility with an average electricity cost of 0.045/kWh. Therefore, the total value of the FCI for the integral methanol plant is around \$38.52 million.

The distribution of unit capital costs for the integral methanol production facility shows that the contribution from wind-based H₂ is the highest (Fig. 7). The production cost of H₂, which makes the $NPV = 0$, is \$1.37/kg H₂ when the selling price of methanol is \$600/mt with the corresponding values of $EC = 0.87$ (< 1) and $PC = 658.25$ /mt methanol ($> \$600$ /mt). Global prices of methanol change widely; the prices as of July 2015 are \$403/mt in Europe, \$442/mt in North America, and \$375/mt in Asia Pacific [58].

The cost of renewable hydrogen and the selling price of methanol affect the economics of the renewable methanol. We have evaluated the final NPV for varying methanol prices and hydrogen prices, the results can be seen in Fig. 9a. The minimum selling price of methanol was also investigated with varying hydrogen production cost (seen in Fig. 9b). This is the selling price of methanol that makes the $NPV = 0$ after 10 years. The inclusion and exclusion of O₂ sales was also investigated in Fig. 9b. A summary of the minimum selling price of methanol versus H₂ production cost can be seen in Table 8.

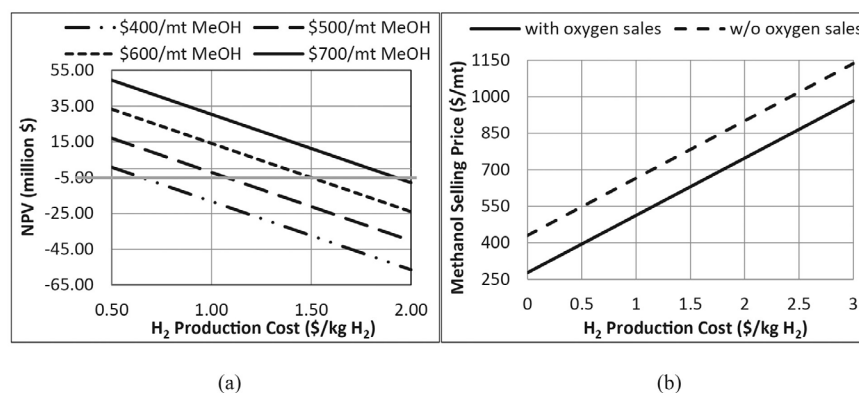


Fig. 9. The influence of H₂ production cost on: (a) net present value at constant methanol (MeOH) price, (b) Selling price of methanol for NPV = 0 with and without selling O₂ byproduct at \$100/mt.

Table 8. Effect of methanol selling price on the maximum unit production cost of renewable hydrogen (NPV = 0 after 10 years).

MeOH price (\$/mt)	H ₂ cost (\$/kg)	EC	PC (\$/mt)
375.00	0.41	0.817	432.21
403.00	0.53	0.827	460.45
442.00	0.70	0.838	498.11
512.82	1.00	0.855	571.09
630.50	1.50	0.877	688.75
748.18	2.00	0.893	806.43
983.54	3.00	0.915	1041.79

The general trends in these graphs indicate that a higher selling price for methanol raises the cost of hydrogen at which the process becomes feasible (NPV > 0). It also indicates that the sale of the O₂ byproduct could be crucial to the economic feasibility of the process. The price of methanol at the DOE's targeted production cost of \$2/kg H₂ [31, 32] is higher than current pricing of methanol. However, methanol pricing is in the ballpark of current rates using the IEA's target of \$0.30/kg H₂ [33, 35].

Renewable hydrogen-based methanol would recycle carbon dioxide as a possible alternative fuel to diminishing oil and gas resources [59]. There are already vehicles which can run with M85, a

fuel mixture of 85% methanol and 15% gasoline [1, 11]. Methanol can be used with the existing distribution infrastructure of conventional liquid transportation fuels. In addition, fuel cell-powered vehicles are also in a fast developing stage, although they are not yet available commercially [1, 2, 15]. Technological advances such as these would lead to a "methanol economy" [11–15].

6.3. Multi-criteria decision matrix

Beside the economic analysis, sustainability metrics should also be used to evaluate the feasibility of chemical processes [60, 61]. For this purpose, Table 9 shows a multi-criteria Pugh decision matrix [62] to assess the renewable and nonrenewable methanol production facilities. The matrix generates the number of plus, minus, overall total, and overall weighted total scores. The weighted total adds up the scores times their respective weighting factors. The weight factors can be adjusted with respect to the location, energy policies, and energy costs and security. The totals are guidance only for decision making. If the two top scores are very close, then they should be examined more closely to make a more informed decision. Renewable energy-based systems may require the combined use of scenario building and participatory multi-criteria analysis for sustainability assessment [61].

Table 9. Multi-criteria decision matrix for feasibility assessment of chemical processes and energy systems.

Economics and sustainability indicators	Weighting factor: 0–1	Fossil-methanol	Non-fossil-methanol
Economic indicators			
Net present value NPV	1	+	–
Payback period PBP	0.8	+	–
Rate of return ROR	0.8	+	–
Economic constraint EC	0.9	+	–
Impact on employment	1	+	+
Impact on customers	1	+	+
Impact on economy	1	+	+
Impact on utility	0.7	–	+
Sustainability indicators			
Material intensity	0.7	–	+
Energy intensity	0.8	+	–
Environmental impact GHG in production	0.8	–	+
Environmental impact GHG in utilization	0.8	–	–
Toxic/waste material emissions-Process safety and Public safety	1	–	+
Potential for technological improvements and cost reduction	0.8	–	+
Security/reliability	0.9	–	+
Political stability and legitimacy	0.8	–	+
Quality of life	0.8	–	+
Total positive score		8	11
Total minus score		–9	–6
Net score (positive-minus)		–1	+5
Weighted total score		+0.2	+5.4

With the weight factors adapted and the combined economic and sustainability indicators, the decision matrix in Table 9 shows that overall weighted score is around +5.4 for the renewable integral methanol facility, which is higher than that of fossil fuel based methanol. This may display the impact of sustainability indicators on evaluating the feasibility of chemical processes requiring large investments and energy resources.

7. Conclusions

Use of wind energy-based hydrogen and CO₂ for methanol synthesis may lead to the reduction in carbon emissions either by recycling and/or fixation. The cost of renewable hydrogen production plays an important role within the economics and determines the scope of technological improvements for electrolytic hydrogen-based methanol production. With current methanol prices hydrogen production costs are required to be between \$0.40 to \$0.70/kg of H₂, for the NPV = 0. More research is required in electrolysis technologies to reduce hydrogen production. However, we have shown the sale of product oxygen from electrolysis could play an

important role in improving economic feasibility. Further work is needed for identifying possible low cost back-end processes that could convert the product methanol into value added chemicals. A life cycle assessment of these chemicals could be conducted to show how much of the CO₂ is ultimately fixed and the overall sustainability of the process. Additionally, further improvements in process integration for hydrogen and CO₂ supply into methanol synthesis would have a positive impact of hydrogen and methanol economies. A multi-criteria decision matrix, containing the economics and sustainability indicators, has been introduced for a more comprehensive feasibility assessment. This matrix may help account for the cost of environmental damage from using fossil fuels in the overall assessment of feasibility. It also shows that although chemical processes using non-fossil fuels may be limited economically these more environmentally conscious processes may achieve better overall assessment scores. This is in line with the need for a better assessment of chemical processes and energy technologies in order to address the sustainability within the context of global challenges of energy security, climate change, and technological advancement.

Appendix

Table A1. Estimated U.S. average levelized cost of electricity (LCE) with 2012 \$/MWh for renewable advanced generation resources entering service in 2019 [1,2].

Plant type	Capacity factor (%)	LCE	O & M with fuel	Transmission investment	Total LCE
Geothermal	92	34.2		1.4	47.9
Biomass	83	47.4	39.5	1.2	102.6
Wind	35	64.1		3.2	80.3
Wind-offshore	37	175.4		5.8	204.1
Solar PV	25	114.5		4.1	130.0
Solar thermal	20	195.0		6.0	243.1
Hydro	53	72.0	6.0	2.0	84.5

O & M: Operations and Maintenance cost; PV: Photovoltaic.

Table A2. Unit energy cost for various utilities with energy source of natural gas for 2014 [23].

Utilities	Energy price, \$/MJ	T_{in} °C	T_{out} °C	Factor ^a	U^b kW/m ² K
Electricity	\$0.0775/kW h			0.58	
Cooling Water	\$0.09/mt	20	25	1	3.75
Steam (MP)	2.2×10^{-3}	175	174	0.85	6.00
Steam (HP)	2.5×10^{-3}	250	249	0.85	6.00

a. CO₂ energy source efficiency factor.

b. Utility side film coefficient for energy analysis.

Table A3. Stream tables highlighting the input and output streams for the methanol production facility.

	H ₂ -IN	CO ₂ -IN	Methanol	Water	Net-flue	BFW	Steam
Temperature °C	25	25.6	25	25	24.9	233	233
Pressure bar	33	16.422	1.013	1.013	1.013	30	30
Vapor frac	1	0	0	0	1	0	1
Mole flow kmol/hr	383.676	131	126.421	126.106	9.077	214.575	214.575
Mass flow mt/day	18.563	138.367	97.011	54.643	5.284	92.775	92.775
Volume flow cum/hr	293.911	5.473	5.093	2.294	221.683	5.097	266.687
Enthalpy Gcal/hr	0.003	-12.817	-7.333	-8.702	-0.44	-13.84	-12.103
Mass fraction							
CO ₂		1	0.002	Trace	0.86		
CO					Trace		
H ₂	1		Trace		0.037		
H ₂ O			0.003	0.995	0.004	1	1
Methanol			0.995	0.005	0.098		
Mole fraction							
CO ₂		1	0.001	Trace	0.474		
CO					Trace		
H ₂	1		6 PPB		0.446		
H ₂ O			0.006	0.997	0.006	1	1
Methanol			0.993	0.003	0.074		

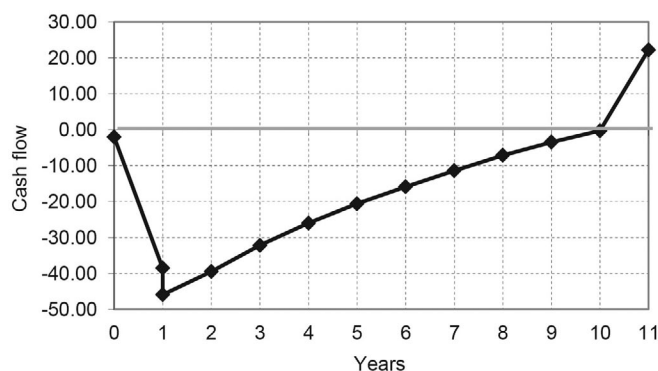


Fig. A1. Plot of the discounted cash flow of the integral methanol plant over 10 years of operation with H₂ selling price = \$0.30/kg H₂; methanol selling price \$485/mt methanol. *CDCF: Cumulative Discounted Cash Flow; FCI: Fixed capital investment = \$38.5 M; WC: Working capital = \$7.7 M; D: Depreciation (Maximum accelerated Cost Recovery System); R: Revenue = \$20.04 M; COP: Cost of production = \$13.99 M; L: Cost of land = \$2 M; S: Salvage value = \$9.85 M; NPV: Net present value; t : tax = 35%, and i : interest rate of bank loan = 5.25%.

Table A4. Calculated values of the economic decision factors from the above DCFD.

EC	0.635
PC, \$/mt	406.32
NPV, M\$	22.22
ROR, %	26.95
PBP, years	7.52

Cost Calculations

$$\text{Cost of Production} = 0.18\text{FCI} + 2.73(\text{COL}) + 1.23 (\text{CRM} + \text{CWM} + \text{CUT}) \quad (\text{A1})$$

where: COL= Cost of Labor; CRM= Cost of Raw Materials;
CWM= Cost of Waste Management; CUT = Cost of Utilities

$$\text{Revenue} = (\text{MeOH}_{\text{price}} \text{MeOH}_{\text{flow}} + \text{O}_2 \text{price} \text{O}_2 \text{flow} + \text{CO}_2 \text{credit}) \times \text{Hours of operation per year} \quad (\text{A2})$$

$$\text{Plant Capacity} = \text{Hours of operation per year} \times \text{Hourly production of methanol} \quad (\text{A3})$$

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References

- [1] Demirel Y. Energy; production, conversion, storage, conservation, and coupling. London: Springer; 2012. <http://dx.doi.org/10.1007/978-1-4471-2372-9>
- [2] U.S. Energy Information Administration. Annual energy outlook. 2014. Retrieved August 5, 2014, from: <http://www.eia.gov/forecasts/aeo/>
- [3] Lantz E, Hand M, Wiser R. 2010 Wind technologies market report. 2011. Retrieved August 20, 2014, from: http://www1.eere.energy.gov/wind/pdfs/2011_wind_technologies_market_report.pdf
- [4] Esmaili P, Dincer I, Naterer G. Energy and exergy analyses of electrolytic hydrogen production with molybdenum-oxo catalysts. Int J Hydrogen Energy 2012;37:7365–72. <http://dx.doi.org/10.1016/j.ijhydene.2012.01.076>
- [5] Tremel A, Wasserscheid P, Baldauf M, Hammer T. Techno-economic analysis for the synthesis of liquid and gaseous fuels based on hydrogen production via electrolysis. Int J Hydrogen Energy 2015, February 12. <http://dx.doi.org/10.1016/j.ijhydene.2015.01.097>
- [6] Dincer I, Ratlamwala T. Development of novel renewable energy based hydrogen production systems: a comparative study. Energy Convers Manag 2013;72:77–87. <http://dx.doi.org/10.1016/j.enconman.2012.08.029>
- [7] Dingizian A, Hansson J, Persson T, Svensson Ekberg H, Tuna P. A feasibility study on integrated hydrogen production. 2007. Retrieved August 10, 2014, from: <http://www.chemeng.lth.se/ket050/Finalreport/HydroHydrogen.pdf>
- [8] Norsk Electrolyzer, Retrieved August 10, 2014, from: http://large.stanford.edu/courses/2010/ph240/pushkarev2/docs/norsk_electrolysers.pdf
- [9] James BD, Moton JM, Colella WG. Guidance for filling out a detailed h2a production case study [Presentation Slides]. 2013. Retrieved August 10, 2014, from: http://energy.gov/sites/prod/files/2014/03/f12/webinarslides_h2a_production_analysis_070913.pdf
- [10] Galindo CP, Badr O. Renewable hydrogen utilisation for the production of methanol. Energy Convers Manag 2007;48:519–27. <http://dx.doi.org/10.1016/j.enconman.2006.06.011>
- [11] Olah GA, Goepfert A, Surya GK. Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons. J Org Chem 2009;74:487–98. <http://dx.doi.org/10.1021/jo801260f>
- [12] Demirel Y, Matzen M, Winters C, Gao X. Capturing and using CO₂ as feedstock with chemical looping and hydrothermal technologies. Int J Energy Res 2015;39:1011–47. <http://dx.doi.org/10.1002/er.3277>
- [13] Jiang Z, Xiao T, Kuznetsov VL, Edwards PP. Turning carbon dioxide into fuel. Philosophical Trans R Soc A 2010;368:3343–64. <http://dx.doi.org/10.1098/rsta.2010.0119>
- [14] Olah GA, Goepfert A, Surya Prakash GK. Beyond oil and gas: The methanol economy. 2 ed. New York: Wiley; 2011
- [15] Faberi S, Paolucci L, Velte D, Jimenez I. Methanol: a future transport fuel based on hydrogen and carbon dioxide? Economic viability and policy options. Brussels: Science and Technology Options Assessment; 2014. <http://dx.doi.org/10.2861/57305>
- [16] Rihko-Struckmann LK, Peschel A, Hanke-Rauschenbach R, Sundmacher K. Assessment of methanol synthesis utilizing exhaust CO₂ for chemical storage of electrical energy. Industrial Eng Chem Res 2010;49:11073–8. <http://dx.doi.org/10.1021/ie100508w>
- [17] Van-Dal ES, Bouallou C. Design and simulation of a methanol production plant from CO₂ hydrogenation. J Clean Prod 2013;57:38–45. <http://dx.doi.org/10.1016/j.jclepro.2013.06.008>
- [18] Van-Dal ES, Bouallou C. CO₂ abatement through a methanol production process. Chem Eng Trans 2012;29:463–8. <http://dx.doi.org/10.3303/CET1229078>
- [19] Pontzen F, Liebner W, Gronemann V, Rothaemel M, Ahlers B. CO₂-based methanol and DME – efficient technologies for industrial scale production. Catal Today 2011;171:242–50. <http://dx.doi.org/10.1016/j.cattod.2011.04.049>
- [20] Mignard D, Sahibzada M, Duthie JM, Whittington HW. Methanol synthesis from flue-gas CO₂ and renewable electricity: a feasibility study. Int J Hydrogen Energy 2003;28:455–64. [http://dx.doi.org/10.1016/S0360-3199\(02\)00082-4](http://dx.doi.org/10.1016/S0360-3199(02)00082-4)
- [21] Martins AA, Mata TM, Costa CA, Sikdar SK. Framework for sustainability metrics. Industrial Eng Chem Res 2006;46:2962–73. <http://dx.doi.org/10.1021/ie060692l>
- [22] Institution of Chemical Engineers. The sustainability metrics: sustainable development progress metrics recommended for use in the process industries. Retrieved August 10, 2014, from http://nbis.org/nbisresources/metrics/triple_bottom_line_indicators_process_industries.pdf; 2004.
- [23] Aspen Technology, Inc. Burlington, MA, USA: Aspen Plus; 2014.
- [24] Official Journal of the European Commission. European commission decision 2007/589/EC. 1–4. 2007. Retrieved August 15, 2014, from: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2007:229:0001:0085:EN:PDF>

- [25] Environmental Protection Agency. EPA Rule E9-5711: federal register/vol. 74, No. 68/2009/Proposed Rules, pp 16639–16641. Retrieved August 12, 2014, from: http://epa.gov/climatechange/emissions/downloads/RULE_E9-5711.pdf
- [26] Kothari R, Buddhi D, Sawhney R. Comparison of environmental and economic aspects of various hydrogen production methods. *Renew Sustain Energy Rev* 2008; February;12:553–63. <http://dx.doi.org/10.1016/j.rser.2006.07.012>
- [27] Mueller-Langer F, Tzimas E, Kaltschmitt M, Peteves S. Techno-economic assessment of hydrogen production processes for the hydrogen economy for the short and medium term. *Int J Hydrogen Energy* 2007; November;32: 3797–810. <http://dx.doi.org/10.1016/j.ijhydene.2007.05.027>
- [28] Wan W, Dai Z, Li C, Yu G, Wang F. Innovative concept for gasification for hydrogen based on the heat integration between water gas shift unit and coal-water-slurry gasification unit. *Int J Hydrogen Energy* 2014;39:7811–8. <http://dx.doi.org/10.1016/j.ijhydene.2014.03.032>
- [29] Dodds PE, McDowall W. A review of hydrogen production technologies for energy system models. UKSHEC Working Paper No. 6. UCL Energy Institute. University College London; 2012.
- [30] Holladay J, Hu J, King D, Wang Y. An overview of hydrogen production technologies. *Catal Today* 2009;139:244–60. <http://dx.doi.org/10.1016/j.cattod.2008.08.039>
- [31] Saur G. Wind-to-hydrogen project: electrolyzer capital cost study. Golden, CO: National Renewable Energy Laboratory; 2008. <http://www.nrel.gov/hydrogen/pdfs/44103.pdf>
- [32] Saur G, Ainscough C, Harrison K, Ramsden T. Hour-by-hour cost modeling of optimized central wind-based water electrolysis production [Presentation Slides]. Golden, CO: National Renewable Energy Laboratory; 2013. http://www.hydrogen.energy.gov/pdfs/review11/pd085_saur_2011_p.pdf
- [33] International Energy Agency. Hydrogen production and storage: R&D priorities and gaps. 2006. Retrieved August 20, 2014, from: <https://www.iea.org/publications/freepublications/publication/hydrogen.pdf>
- [34] Penev M. Hybrid hydrogen energy storage. National Renewable Energy Laboratory; 2013. Retrieved August 10, 2014, from: <http://www.h2fcsupergen.com/wp-content/uploads/2013/06/Hybrid-Hydrogen-Energy-Storage-Michael-Penev-National-Energy-Research-Laboratory.pdf>
- [35] International Energy Agency. Technology roadmap: energy and GHG reductions in the chemical industry via catalytic processes. 2013. Retrieved August 10, 2014, from: http://www.iea.org/publications/freepublications/publication/Chemical_Roadmap_2013_Final_WEB.pdf
- [36] Finely R. Evaluation of CO₂ capture options from ethanol plants. Illinois State Geological Survey; 2006. http://sequestration.org/resources/publish/phase2_capture_topical_rpt.pdf
- [37] Grant T. Carbon dioxide transport and storage costs in NETL studies. National Energy Technology Laboratory; 2013. Retrieved August 05, 2014, from: http://www.netl.doe.gov/File%20Library/Research/Energy%20Analysis/Publications/QGESS_CO2T-S_Rev3_20140514.pdf
- [38] Economic Indicators. Chemical engineering essentials for the CPI professional. 2015. p. 72. <http://www.chemengonline.com/>
- [39] Martin O, Perez-Ramirez J. New and revisited insights into the promotion of methanol synthesis catalysts by CO₂. *Catal Sci Technol* 2013;3:3343–52. <http://dx.doi.org/10.1039/c3cy00573a>
- [40] Bansode A, Urakawa A. Towards full one-pass conversion of carbon dioxide to methanol and methanol-derived products. *J Catal* 2014;309:66–70. <http://dx.doi.org/10.1016/j.jcat.2013.09.005>
- [41] Hoekman S, Broch A, Robbins C, Purcell R. CO₂ recycling by reaction with renewably-generated hydrogen. *Int J Greenh Gas Control* 2010;4:44–50. <http://dx.doi.org/10.1016/j.ijggc.2009.09.012>
- [42] Wang W, Wang S, Ma X, Gong J. Recent advances in catalytic hydrogenation of carbon dioxide. *Chem Soc Rev* 2011;40:3703–27. <http://dx.doi.org/10.1039/C1CS15008A>
- [43] Lim H-W, Park M-J, Kang S-H, Chae H-J, Bae J, Jun K-W. Modeling of the kinetics for methanol synthesis using Cu/ZnO/Al₂O₃/ZrO₂ catalyst: influence of carbon dioxide during hydrogenation. *Industrial Eng Chem Res* 2009;48: 10448–55. <http://dx.doi.org/10.1021/ie901081f>
- [44] Studt F, Sharafutdinov I, Abild-Petersen F, Elkjaer CF, Hummelshøj JS, Dahl S, et al. Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol. *Nat Chem* 2014;6:320–4. <http://dx.doi.org/10.1038/nchem.1873>
- [45] Yang C-J, Jackson RB. China's growing methanol economy and its implications for energy and the environment. *Energy Policy* 2012;41:878–84. <http://dx.doi.org/10.1016/j.enpol.2011.11.037>
- [46] Toyir J, Miloua R, Elkadri N, Nawdali M, Toufik H, Miloua F, et al. Sustainable process for the production of methanol from CO₂ and H₂ using Cu/ZnO-based multicomponent catalyst. *Phys Procedia* 2009;2:1075–9. <http://dx.doi.org/10.1016/j.phpro.2009.11.065>
- [47] Machado CF, de Medeiros JL, Araujo OF, Alves RM. A comparative analysis of methanol production routes: synthesis gas versus CO₂ hydrogenation. In: Proceedings of the 2014 International Conference on Industrial Engineering and Operations Management. Bali: Indonesia; 2014. p. 2981–90.
- [48] Graaf G, Stamhuis E, Beenackers A. Kinetics of low-pressure methanol synthesis. *Chem Eng Sci* 1988;43:3185–95. [http://dx.doi.org/10.1016/0009-2509\(88\)85127-3](http://dx.doi.org/10.1016/0009-2509(88)85127-3)
- [49] Weiduan S, Zhang J, Bingchen Z, Hongshi W, Dingye F, Mingjia Z, et al. Kinetics of methanol synthesis in the presence of C301 Cu-based catalyst (i) intrinsic and global kinetics. *J Chem Industry Eng* 1989;4:248–57 [China].
- [50] Bykov A, Rubin M, Sul'man M, Sul'man E. Liquid-phase methanol synthesis in the low pressure field. *Biocatalysis* 2014;6:143–9. <http://dx.doi.org/10.1134/S2070050414020020>
- [51] Vanden Bussche K, Forment G. A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al₂O₃ catalyst. *J Catal* 1996;161:1–10. <http://dx.doi.org/10.1006/jcat.1996.0156>
- [52] Li C, Yuan X, Fujimoto K. Development of highly stable catalyst for methanol synthesis from carbon dioxide. *Appl Catal A General* 2014;469:306–11. <http://dx.doi.org/10.1016/j.apcata.2013.10.010>
- [53] Clausen LR, Houbak N, Elmegaard B. Technoeconomic analysis of a methanol plant based on gasification of biomass and electrolysis of water. *Energy* 2010;35:2338–47. <http://dx.doi.org/10.1016/j.energy.2010.02.034>
- [54] Skrzypek J, Lachowska M, Moroz H. Kinetics of methanol synthesis over commercial copper/zinc oxide/alumina catalysts. *Chem Eng Sci* 1991;46: 2809–13. [http://dx.doi.org/10.1016/0009-2509\(91\)85150-V](http://dx.doi.org/10.1016/0009-2509(91)85150-V)
- [55] Chen L, Jiang Q, Song Z, Posarac D. Optimization of methanol yield from a Lurgi reactor. *Chem Eng Technol* 2011;34:817–22. <http://dx.doi.org/10.1002/ceat.201000282>
- [56] Anicic B, Trop P, Goricanec D. Comparison between two methods of methanol production from carbon dioxide. *Energy* 2014;77:279–89. <http://dx.doi.org/10.1016/j.energy.2014.09.069>
- [57] Turton R, Bailie RC, Whiting WB, Shaeiwitz JA, Bhattacharyya D. Analysis, synthesis and design of chemical processes. 4 ed. Upper Saddle River: Prentice Hall; 2012.
- [58] Methanex. Current Posted Prices. Retrieved July 9, 2015, from <https://www.methanex.com/our-business/pricing>
- [59] Luk H, Lei H, Ng W, Ju Y, Lam K. Techno-economic analysis of distributed hydrogen production from natural gas. *Chin J Chem Eng* 2012;20:489–96. [http://dx.doi.org/10.1016/S1004-9541\(11\)60210-3](http://dx.doi.org/10.1016/S1004-9541(11)60210-3)
- [60] Demirel Y. Sustainable operations for distillation columns. *Chem Eng Process Tech* 2013;1005:1–15.
- [61] Kowalski K, Stagl S, Madlener R, Omann I. Sustainable energy futures: Methodological challenges in combining scenarios and participatory multicriteria analysis. *Eur J Operational Res* 2009;197:1069–74. <http://dx.doi.org/10.1016/j.ejor.2007.12.049>
- [62] Pugh S. Concept selection: a method that works. In: Proceedings International Conference on Engineering Design. Zurich: Heurista; 1981. p. 497–506.