Simulation of Biomethanol Production from Green Syngas Through Sustainable Process Design

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Abstract: Methanol is considered an alternative energy source due to its various applicability and high octane. As a fuel, it releases low emissions, and shows high performance and low risk of flammability. Egypt faces a high population growth rate, which implies an increase in the agricultural production. At present, the agriculture waste materials are burned leading to major environmental problems besides the loss of potential resources. This work builds a design methodology for producing biomethanol fuel from green syngas. The design methodology is based on rigorous model using the Aspen HYSYS® simulation software, and takes into account both economics and environment. As a case study, the design methodology is applied to design a plant that converts rice straw in Egypt into methanol. The raw materials for this process are selected from the major regions in Egypt producing rice straw with a total capacity of 1.6 million tons per year. These local regions are Kafr el Sheikh, Dakahlia and Sharkia governorates, located in northern part to Cairo. The methanol produced from the process is estimated to be around 156 thousand metric tons per annum. The process equipment capital costs are estimated to be 498 million dollars with total energy costs of 17 million dollars per annum. On the other hand, an annual revenue of 537 million dollars is obtained. The simulation model obtained in this study can be applied to any syngas coming from other gasification processes with different biomass feedstock. In addition, the model provides a robust basis for further studies of process integration leading to innovative and sustainable solutions to climatic and energy problems.

1 INTRODUCTION

Major environmental and economic problems as global warming, climatic changes, and oil prices fluctuating are caused by fossil fuels. These facts drive the energy sector towards finding sustainable and innovative solutions. Biofuels arose as an effective alternative for the fossil fuels as a cleaner renewable source of energy with fewer environmental impacts. Thinking of new process designs to reach sustainable goals is a challenge that all industries must face.

Second generation biofuels derived from lignocellulosic feedstocks are promising alternative for energy that concerns environment (Damartzis and Zabaniotou, 2011). Many innovative technologies such as gasification and Fischer–Tropsch synthesis created many opportunities for thermochemical conversion of biomass into biofuels. Gasification is considered as ancient as combustion, although it is less developed since combustion is dominant in its applications. Recently, the

significance of gasification has grown up to convert biomass into gas or liquid valuable materials. The motivating factors of gasification can be summarized as its renewability, environmental consciousness and sociopolitical benefits (Basu, 2010). As a result, different gasifier designs differing in the biomass pyrolysis and tar cracking mechanisms have been evolved. Researchers have conducted different experimental setups and changed various parameters via gasification on different biomass feed stocks (Mertzis et al., 2014; Olgun et al., 2011; Patil et al., 2011; Simone et al., 2013; Xie et al., 2014).

It was stated by the Egyptian Central Agency for Public Mobilization and Statistics (CAPMAS, 2012) that the rice production in Egypt rose 31.2% in the year 2011 reaching some 5.6 million tons, compared with 4.3 million tons for 2010. Experts say that such a production will generate more than 30 million tons of waste per year. This will consequently lead to major environmental problems as these wastes are currently burned leading to what is called the black

cloud phenomena experienced in Egypt recently. Finding solutions to such problem is a critical issue.

Methanol is considered as a liquid fuel that can be used in fuel cells and as a chemical feed-stock in addition to its use as a transportation liquid fuel (Yang et al., 2004). Most methanol plants built all over the world use natural gas for generation of syngas to produce methanol. The scope of process system engineering is increasing so as to achieve more sustainable processes (Jegatheesan et al., 2009). Design of plants converting biomass to methanol is challenging; most existing design approaches are just in the form of simulations to the process and have not been commercialized yet. Few researches (Abu Bakar et al., 2013; Bula et al., 2012; Kumabe et al., 2008; Shabangu et al., 2014) have simulated the methanol production from different biomass feed stocks. The syngas required to produce biomethanol could be attained from the process that includes pre-treatment of the biomass, gasification according to the biomass physical characteristics, cleaning of the gas produced, and the final methanol catalytic synthesis (Minteer, 2006). It is obvious that tackling the environmental problems of biomass residues is essential and requires design methodologies and procedures.

The objective of this work is to build a design methodology for producing methanol from biomass. The new design methodology is rigorous simulation-based and applicable to methanol production from any source of biomass. Aspen Hysys simulator (Hysys User Guide, 2004) is adopted to model the production plant. The simulation model achieved in the study is robust and can help for further investigation studies, such as optimization, process integration, dynamic control, sensitivity analysis, scaling, etc. As a case study, the design methodology is applied to design a plant that produces methanol from rice straw in Egypt.

2 DESIGN AND SIMULATION METHODOLOGY

Conventionally biomethanol is produced from the synthesis gas that is rich in hydrogen and carbon monoxide through a heterogeneous catalysis mechanism. Figure 1 shows the ordinary process flow schematic diagram for biomethanol production from biomass gasification (Ohlstrom, 2001). In this study some critical points are identified during the process design: The low purity of H_2 in the waste gas stream seems to be unsuitable for reuse. Thus,

purification of this H_2 stream can be considered. Also, the CO_2 circulating in the process demands high amount of energy. This calls for removal from the syngas stream. Further, the presence of water circulating in the process leads to high energy wastage. This also calls for purification of the syngas stream. Hence, the following structural modifications are proposed based on the above recommendations: installation of a separation unit to improve the H_2 purity in the waste gas stream and purification of the syngas feed stream by removing CO_2 and water components.

In this design the Aspen HYSYS Ver. 7.3 process simulator is used to model the given process. Other process simulators can be employed such as Aspen Plus, PRO/II, VMG, etc. The given process is simulated on the basis of converting a certain amount of syngas into green methanol fuel. In this stage the feed streams are specified, and the flow process design is described, further mass and energy balances are performed. Finally individual process equipments are designed. As a result of this stage, temperatures, pressures, and flows of all process streams and products are obtained in addition to equipment dimensions, and heat and cooling duties.

Process economics is considered in the proceeding stage. Equipment capital costs, total utilities costs, and raw material costs are estimated. Finally the total profit is calculated. CAPCOST, a powerful tool for evaluating full process economics and profitability is used (Turton et al., 2009). In this stage it is easy to assess the process feasibility.

After reaching a base case design with the associated economics, the environmental implications of the process is to be considered consciousnessly. In this stage of design emissions from the process is to be estimated also the potential characterization of waste water is to be considered. The aim of this stage is to reduce the local and global CO_2 emissions in addition to minimizing the release of harmful compounds from the process to the atmosphere.

While the environment is considered in the earlier phase, the energies of all process streams are to be integrated with the objective of minimizing the energy demands of all the process. Pinch Analysis and heat integration principles are to be applied to attain the best heat exchanger network (HEN) where minimum amount of utility requirements are required. An ideal solution of this phase is an optimum heat integrated process.

Either the base case design or the environmental based design is to be optimized by manipulating the

operating and design parameters of the process to minimize multiple objectives. These optimization objectives may include the total costs, utility requirements, CO_2 emissions or any other objective. The sections below detail the new design methodology.
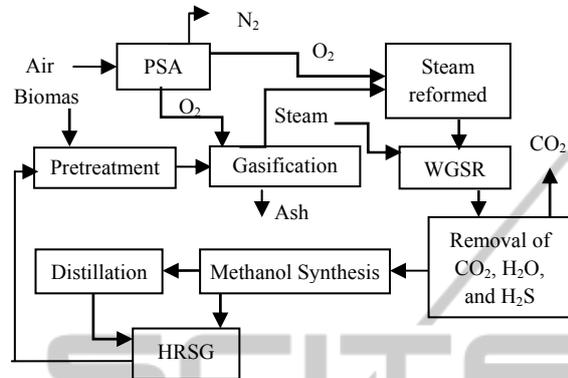

Figure 1: Schematic for biomethanol production from biomass.

2.1 Simulation Procedure and Algorithm

Figure 2 summarizes the simulation algorithm for biomethanol production from biomass. As shown in the figure the algorithm illustrates the main phases of simulation design. It starts by the biomass gasification reaching the green syngas production, and then follows to the process simulation part through the model validation, analysis, costing and optimization. More details will be presented in the following sections.
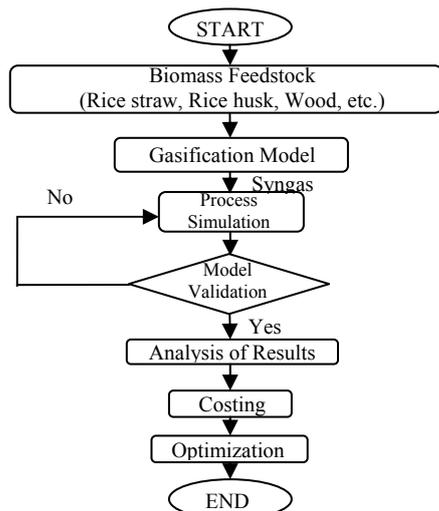

Figure 2: Simulation algorithm for methanol production from biomass.
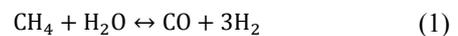
2.2 Syngas Adjustment Stage

Methanol is one of the most important basic chemicals that can be produced using synthesis gas (a mixture of CO, CO_2 and H_2). The typical methanol process involves a reaction of syngas in the presence of metal catalyst followed by purification of the methanol. Here the feed is syngas produced from biomass gasification which totally differs from the syngas coming from the natural gas in properties and conditions. The high percentage of nitrogen found in the gas has to be separated first, and then the syngas is sent to the reformer to convert the existing methane to extra syngas. Water gas shift reactor adjusts the reactor feed requirements by providing the required amount of hydrogen through the water gas shift reaction. Water and CO_2 are removed, and then the make-up stream is ready to be mixed with the recycle stream, and further fed to the reactor. In one pass only, thermodynamic equilibrium is reached before achieving 50% conversion of the synthesis gas, therefore, after methanol and water are condensed out and removed, the remaining synthesis gas must be recycled to the reactor. Adjustment stages are discussed in this section.

2.2.1 Nitrogen Separation

Pressure swing adsorption (PSA) can be a cost-effective method of onsite nitrogen generation for a wide range of purity and flow requirements. So it is used to separate 97.5 mole% of nitrogen that exists; separation is assumed to be ideal in which the separated nitrogen stream is pure nitrogen.

2.2.2 Methane Reformer

Since most biomass gasifiers produce significant amount of methane and small amounts of other light hydrocarbons, it is wise to use them to produce extra amount syngas through steam reforming. The reaction is carried out according to the following highly endothermic reaction:

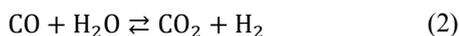$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (1)$$

Acceptable conversion is achieved only at relatively high temperatures (>800°C), conventional steam reformers operate at temperature of up to 1000°C. Since the total number of moles of gas increases significantly throughout the reaction, reforming is also favored at lower pressures (1-3.5MPa). Methane conversion in biomass systems varies from 60-90% using Ni-based catalyst. Steam is required not only for promoting the reaction but

also to prevent carbon formation (coking), for that steam to carbon ratio are recommended to be $\geq$ 3:1 which is achieved in the model.

2.2.3 Water Gas Shift Reactor

Syngas out of the reformer is then cooled before being sent to a shift reactor that converts CO to H_2 via the water-gas shift reaction:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (2)$$

For methanol synthesis, the shift reactor is used to increase H_2 to CO ratio which is found to be essential in this process. Since the shift reaction is exothermic, higher conversion levels are achieved at lower temperatures. The reaction nearly proceeds to completion with modern catalysts (ZnO-CuO) at temperatures as low as 200°C. In this process, only 60% conversion is required to achieve the purpose of having proper hydrogen amount in the make-up gas. The water gas shift reactor (WGSR) operates at 200°C, design parameters is adjusted to reach the required conversion. In this model no steam was added to the shift reactor, the amount of steam in the feed was already sufficient due to the extra steam added in the reformer.

2.2.4 Water Removal

To reduce the water content in the syngas stream, a condensation-separation process was proposed. At pressure of 13 bar cooling the water to 110 °C is necessary so as to condense only the water rather than other compounds flowing in the stream.

2.2.5 CO₂ Removal

The CO hydrogenation reaction is considered to be the primary reaction in methanol formation. CO_2 hydrogenation reaction results in the loss of some of the hydrogen as water that is why in ideal circumstances there would be no CO_2 in the feed. However small amount of CO_2 (1-2%) acts as a promoter of the primary methanol synthesis and helps maintain catalyst activity. As a matter of fact, the use of membrane process for CO_2 removal from syngas has been commercially available (Membrane Technology & Research, 2010a). Using such technology, CO_2 recovery with up to 80% at 95% purity on volume basis can be obtained. In this process 85% of the CO_2 found in the gas stream out of the separator is assumed to be removed.

2.2.6 Compression

After leaving the carbon-dioxide membrane, dry syngas enters the syngas compressor at 13 atm where it is compressed to 50 atm, the pressure at which the proposed low pressure Lurgi methanol synthesis reactor operates. Inter-cooling appears between the two compressors so as to decrease the net power consumption.
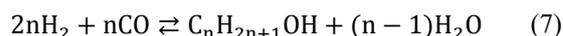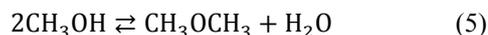
2.2.7 Pre-reactor Heating

After the make-up stream in compressed and mixed with the recycle stream, and before sending the syngas to the methanol reactor, it is heated close to the temperature in the methanol reactor (260°C). This is necessary as temperatures lower than this reaction temperature has the problem of low equilibrium constants (slow reactions). Also catalyst activity drops off sharply below 230°C (Katofsky, 1993).

2.3 Reaction Modeling

Feed syngas enters methanol reactor at temperature of 260 °C and pressure of 50 atm in the presence of metal catalyst most common commercially is the (Cu–ZnO–Al₂O3). Two successive reactions take place in the reactor:

$$CO + 2H_2 \rightleftarrows CH_3OH \qquad (3)$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \qquad (4)$$

Since all of the above reactions are exothermic reactions, heat removal from the reactor is a critical issue. Water gas shift reaction may slightly occur during the methanol synthesis which is ignored in this design. Single pass conversion in the methanol reactor ranges from 40 to 60 percent of CO and CO_2. To increase the conversion, the un-reacted gases after methanol condensation are recycled back to the reactor, in which up to 99.5 percent overall conversion can be achieved (Vaswani, 2000). Although modern methanol synthesis catalysts are highly selective, some side reactions are possible, such as:

$$2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O \qquad (5)$$

$$CO + H_2 \rightleftarrows CH_2O \qquad (6)$$

$$2nH_2 + nCO \rightleftarrows C_nH_{2n+1}OH + (n-1)H_2O \qquad (7)$$

The formation of these species is limited by the selectivity of the catalyst and the kinetics at the reactor conditions. For simplicity, this model considers dimethyl-ether as the only side product in the system; the amount of dimethyl-ether produced

is typically equal 2% wt of the methanol produced. The make-up gas should be slightly hydrogen rich to compensate the hydrogen consumed by reactions and also that is lost in the purge stream. The quantity of hydrogen in the make-up gas stream must satisfy the stoichiometry of both methanol synthesis reactions, and this could be typically determined by the R-value which should be 2 or more:

$$R = \frac{H_2 - CO_2}{CO + CO_2} \geq 2 \qquad (8)$$

Due to hydrogen build up, the actual combined R-value (make-up + recycle) reached more than 4 in this model. Table 1 summarizes all reactors data.

2.4 Product Purification

Stream out of the reactor is cooled to 45°C. CH_3OH, DME and H_2O condense out of the product gases. It is assumed that a complete condensation of these components takes place. Other components entering the condenser leave as gases. Uncondensed gases like CH_4, N_2, un-reacted CO, un-reacted CO_2 and un-reacted H_2 are removed in a flash drum at the top as a purge.

Then part of it (molar recycle ratio approximately 4 of the makeup feed) is recycled back to the reactor and the other part is used to produce the pure hydrogen. The liquid fraction is taken out at the bottom and it mainly consists of CH_3OH, DME and H_2O. A membrane process for H_2 purification has also been widely used in the refineries. The process has been claimed to be able to recover up to 95% of H_2 at 99% purity on volume basis (Membrane Technology & Research, 2010b). Hence, these alternatives were implemented in the HYSYS model of the base case process simulation. In pre-distillation pressure relief valve, the pressure of the outlet stream from the condenser is reduced from 41.4 atm to 11.2 atm for the removal of uncondensed gases and to allow the separation of the DME tower at this operating pressure. Liquid out from the separator post the reactor enters a relief valve in which the pressure is reduced from 41.4 atm

to 11.2 atm for the removal of uncondensed gases and to allow the separation of the DME tower at this operating pressure feed to the distillation column is at the boiling point of DME (45°C) at 11.2 atm. It is assumed that complete recovery of DME takes place in the top product. Water and methanol are assumed to leave as bottoms of DME distillation column at 45°C. Fifteen trays, and with reflux ratio of 20 are able to perform the distillation process. The bottom exit from the DME distillation column consists of CH_3OH and H_2O at 11.6 bar and 157.2°C, the pressure of this stream is first reduced to 3.4 atm (the pressure at which methanol distillation occurs), and then it is cooled to 45°C. The exit stream from pre-methanol distillation column valve enters methanol distillation column at 45°C and 3.4 atm. It is assumed that 99.9 percent recovery of methanol in top product takes place producing 99.9 percent pure methanol on weight basis. Water with a trace quantity of methanol is recovered at the bottom. Forty-five trays, and with reflux ratio of 1.5 are able to perform the distillation process.

The above algorithm and simulation procedure will be applied to address a local environmental problem in north Egypt. A case study will be considered in the following section.

3 CASE STUDY

The raw materials for the case study are selected from the major regions in Egypt producing rice straw with a total capacity of 1.6 million tons per year. These local regions are Kafr el Sheikh, Dakahlia and Sharkia governorates, located in northern part to Cairo (Bakker, 2011). After gasification, the amount of volatile matter which is mainly syngas represents about 60% of the biomass feed (Basu, 2010), so that the synthetic gas feed to methanol synthesis process (from gasifier) can be calculated to be 0.96 million tons per year. In this study 300 operational days are assumed per year. Table 2 and Table 3 show an approximation for the

Table 1: Reactor simulation data.

Reaction	Reactions equations	Conversion (%)	Reactor
Steam Reforming	$CH_4 + H_2O \longrightarrow CO + 3H_2$	85	Steam Reforming
WGSR	$CO + H_2O \longrightarrow CO_2 + H_2$	60	WGSR
CO to Methanol	$CO + 2H_2 \longrightarrow CH_3OH$	50	
CO_2 to Methanol	$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$	50	Methanol Reactor
DME formation	$2CO + 4H_2 \longrightarrow CH_3OCH_3 + H_2O$	5	

syngas compositions and conditions coming from the gasification process respectively (Patil et al., 2011). It is assumed to use Peng-Robinson Fluid package which is commonly used with petrochemical compounds, but it is not recommended by HYSYS when using dimethyl-ether. So the SRK-Twu Fluid package is adopted in the model instead.

Table 2: Syngas composition (Mole percent).

Component	Mole %
CO	22.2
Hydrogen	10.9
Methane	4.5
CO2	11.5
Nitrogen	50.9

Table 3: Syngas conditions.

T (°C)	866
P (atm)	1
Mass Flow rate (kg/hr)	133,333

4 RESULTS AND DISCUSSION

Figure 3 shows the process flow diagram designed in this study for methanol production from synthesis gas generated from the biomass gasification process. The figure shows the most important stages made on the gasifier syngas so as to reach the desired biomethanol product, such as the methane reforming reactor, the water gas shift reactor and the methanol synthesis reactor. The process is rigorously simulated starting from the syngas adjustment stage and reaching to the final product purification stage. This simulation model provides a robust basis for further studies of process integration, environmental assessment, and optimization studies leading to innovative solutions to the energy scarcity problems. Moreover, it can be applied on any type of biomass reaching to liquid methanol production as a sustainable model of a biorefinery. Table 4 shows the methane reformer steam conditions used in the process necessary to convert the methane to syngas with required R-value. The flow rate is adjusted so as there is no need to enter steam in the WGSR. Also, the pressure and temperature conditions are set favoring the methane reforming reaction.

Table 4: Reformer steam conditions.

Flow rate (kgmole/hr)	5770
P (bar)	15
T (°C)	198.5

Economic analysis has been performed for this case with the aid of CAPCOST tool. The methanol obtained is estimated to be around 156 thousand metric tons per year. The process equipment capital costs are estimated to be 498 million dollars with total utilities costs of 17 million dollars per year. On the other hand, revenue of 537 million dollars is obtained per year. Table 5 shows a summary of the costs including capital and energy costs. It is obvious that the operating costs of the process are much lower than its raw material costs. This can show an indication of the profitability of the process. Table 6 shows a summary of the annual revenue obtained from each product production.

Table 5: Summary of costs.

Total Cost of Equipment (MM$)	498
Annual Utilities Cost (MM$/Yr)	17
Cost of Raw Material (MM$)	41.5
Cost of Land (M$)	875

The annual revenue achieved from the methanol which is the main product is estimated to be 81 million dollars. This value covers both the annual operating and raw material costs. Also, the high quantity of nitrogen can be useful if it is sold to nearby plant that can use it in liquefaction purposes as an example. Integration between hydrogen and nitrogen products to produce ammonia (NH_3) can be useful as ammonia serves as an essential precursor to food and fertilizers industries. Finally Figure 4 shows the cash flow diagram for this case illustrating the tremendous increase in the project value after around 4 years from the project life implementation.

Table 6: Summary of revenues.

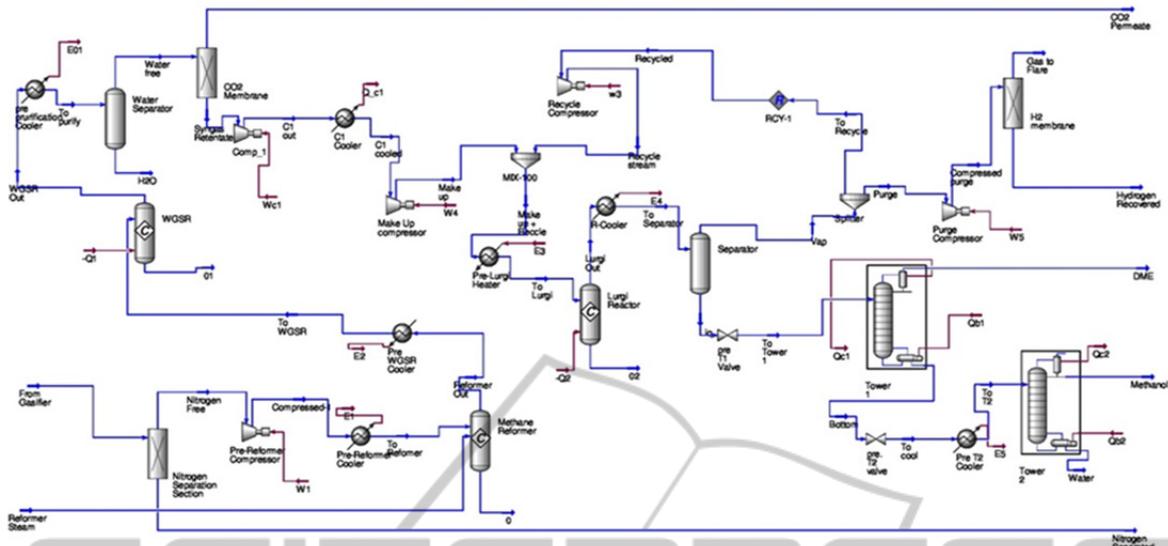| Material Name	Price ($/kg)	Flowrate (kg/h)	Annual Revenue (MM$)
Methanol	0.52	21593	81
Nitrogen	0.85	69972	428
Hydrogen	3.50	670	17
Carbon Dioxide	0.02	50980	7.5
Dimethyl Ether	0.68	655	3.5

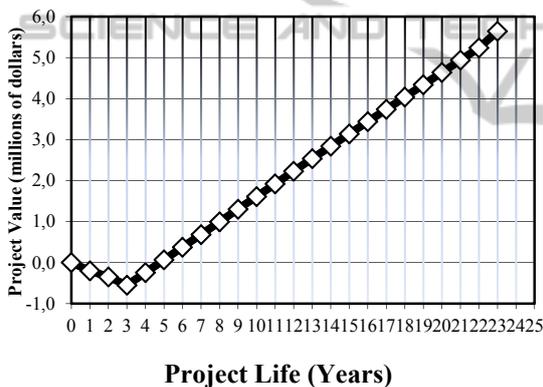Figure 3: Biomethanol production process flow diagram.

Figure 4: Cash flow diagram (Acquired from CAPCOST).

5 CONCLUSIONS

In the present study, a design methodology was developed for producing biomethanol out of the green syngas coming from the biomass gasification route. The design methodology is rigorous simulation-based and can be applied to any source of biomass for methanol production. The design methodology was applied to design a plant that produces methanol from rice straw in Egypt as a case study. In addition, the economic analysis for the case study was investigated. The simulation model achieved is robust; Hence, as a recommendation further investigation studies, such as optimization, process integration, dynamic control, sensitivity analysis, scaling, etc. have to be performed.

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