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Computer aided evaluation of large-scale bio-hydrogen production from empty palm fruit bunches

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Abstract : Nowadays, there are specific needs related to palm oil production chain that must be satisfied in order to achieve sustainability, and one of them is the valorization of residual biomass generated during palm oil production. In this sense, computer-aided simulation has been successfully used to evaluate emerging technologies of biomass processing to obtain high value products and can help to predict technical behavior of novel feedstocks that matches the sustainability criterion. In this work, a valorization of palm oil crop residues through hydrogen production using computer aided process engineering was developed based on a palm production capacity of 360,000 t/yr. Simulation took into account technological limitations and novel equipment performance, special chemical species present in bunches were modeled and process topology was built using a commercial simulation software. A sensitivity analysis was performed by changing relevant operating conditions in the hydrogen production process. Results shows that, with the biotechnological process for hydrogen it can be produced 3989.76 t/yr of hydrogen from Empty Palm Fruit Bunches without using a sulfur removal unit. In addition, it is possible the use of Selexol™ for cleaning the hydrogen and retrieve it at 10 °C and 36.2 atm, which makes unnecessary including a desorption tower.

Keywords : Residual biomass, valorization, emerging technologies, hydrogen.

Introduction

High population growth rate, economic issues, world energy consumption and potential depletion of fossil fuels in the future, make necessary to find renewable alternatives to fuel resources. The abundance and relatively low cost of lignocellulosic materials make them an attractive renewable feedstocks[1]. Syngas is one of the gasification products and emerging alternative fuels that could derive from biomass[2]. It is possible to obtain hydrogen from Empty Palm Fruit Bunches (EPFB) via steam gasification in a fluidized bed gasifier[3]. Hydrogen production based on biomass as raw material can be performed using different hydrogen production technologies[4]. In the last years, most hydrogen is derived from methane using various methods as steam, partial oxidation and autothermal reforming. Although a steam reforming provides the highest hydrogen yield compared with the other reforming processes, it involves a highly endothermic reaction, which requires high external heat source[5]. The aim of this work is develop a hydrogen production process from palm oil crop residues using computer aided process engineering in order to achieve residue valorization.

Process Description

Empty Palm Fruit Bunches (EPFB) produced from the palm oil plantations in the Colombian North Zone was used as feedstock[6]. The plant for hydrogen production was dimensioned to transform an EPFB mass flow of 360,000 t/yr, which is the average quantity produced as a by-product in the industrial process. Computational analysis was made using commercial simulation UniSim Design® package. The system described here is detailed by European Fertilizer Manufacturers' Association (EFMA)[7]. EPFB and coal were used as raw material, biomass composition used in this work is reported in Table 1, which was normalized based on information reported by Mohammed, Salmiaton, Wan Azlina & Mohamad Amran (2012)[8], Ogi, Nakasishi, Fukuda & Matsumoto (2013)[9], Aziz, Prawisudha, Prabowo & Budiman (2015)[10]and Messerle, Ustimenko & Lavrichshev (2016)[11].

Table 1.Composition of Empty Fruit Bunches (EPFB) and Coal used for simulation.

Properties	EPFB (wt%)	Coal (wt%)
Moisture (wb)	55.6	5.8 (total)
Moisture (db)	5.18	0.0
O (db)	45.66	6.56
N (db)	1.21	0.8
C (db)	46.62	48.86
H (db)	6.45	3.05
Ash (wb)	3.45	40
Volatile matter (db)	34.84	26
Sulfur(db)	0.035	0.73

Biomass gasification pre-treatment process.

The process of hydrogen production from empty palm fruit bunches via gasification is presented in Figure 1. In the pre-treatment stage, EPFB is dried from a wet base of 55 % to 5 % at 100 °C. After that, biomass is milled in order to reduce the particle size increasing the heat transfer area and Syngas production efficiency. In gasification stage, entrained-flow biomass gasifier model proposed by Ogi et al. (2013)[9] was selected. $[H_2O]/[C]$ and $[O_2]/[C]$ atomic ratios were established as 2 and 0.35 to increase the formation of Syngas decreasing the formation of solid and liquid co-products (e.g. tars and char) and other gases as methane. In order to carry out an optimum biomass transformation from solid to gas, operation temperature and pressure values were 900°C and 60 bar.

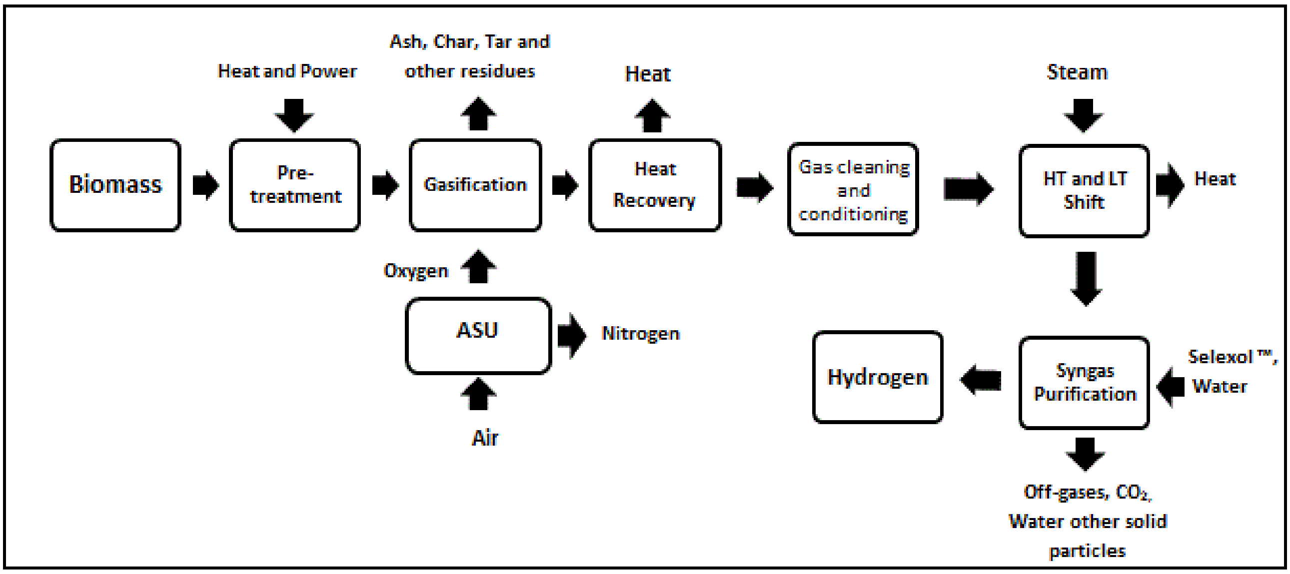

Figure 1. Schematic model of the gasification based hydrogen production

For gasification stage, air enrichment with oxygen is used as gasificant due its lower cost and the less complex engineering necessary to provide the stream following the gasification reaction requirements; but this practice is most effective in process where a high purity Syngas (~ 99.9% H_2) is not necessary, as Integrated Gasification Combined Cycle (IGCC). The gasifier outlet stream is send to a cyclone to separate the suspended solid particles (mainly char). The process inside the reactor was considered isothermal; this means that outlet stream temperature is 900 ºC. An Air Separation Unit (ASU) was simulated to produce the oxygen stream which feed the gasifier. The air stream was assumed as free in argon (79% N_2, 21% O_2) in order to simplify the mass balance and the High-Low distillation columns system complexity.

Heat recovery, gas cleaning and conditioning processes.

In the quench, the gas is cooled to 10 ºC, obtaining a consider quantity of steam which can be applied in driving compressors for energy generation through turbines[12]. After that, CO_2 is removed from the Syngas in a Water Scrubbing Process in order to increase the hydrogen production in the High Temperature Shift (HTS) reactors, which are equilibrium reactors.

High and Low Temperature Shift Reaction.

In order to increase hydrogen concentration of the syngas, a water gas shift (WGS) reactor was carried out. In the shift conversion, the methane is converted into CO_2 and H_2. Low CO_2 content and saturated in water Syngas is heated to reach the shift reactor temperature. HTS reaction yield is highly affected by temperature, [CO]/[H2O] atomic ratio, catalyst activity and the kind of catalyst implemented in the reaction. Catalyst selected for HTS was the commercial catalyst Fe_3O_4/Cr_2O_3[13]. Finally, Syngas is cooled until 270 ºC, in Low Temperature Shift (LTS) stage. The catalyst for this system consists of CuO/ ZnO/ Al_2O_3 in equal portions; and possesses a high activity at low temperatures. The excess of water was eliminated through a flash distillation device at 35 °C and 36.2 bars**.**The process stages mentioned before were simulated in Unisim Design® applying a SRK fluid package.

Syngas Purification.

As Syngas also contains undesirable compounds as particles, condensable tars, alkalis, CO_2, H_2S, HCl, NH_3, COS and HCN, gasifier product stream must be purified and conditioned to produce a gas with suitable conditions. Purification of Syngas also reduces potential problems in subsequent processes, for example, if the hydrogen will be applied in Haber- Bosch Ammonia Process, the presence of acid gases can produce poisoning of the catalysts and obstructions in the equipment[14]. According with the explanation, Acid Syngas has to be removed in order to avoid catalyst poisoning in downstream process (e.g. ammonia or methanol synthesis)[15]. For CO_2 removing stage, Selexol™ process was modeled[16]. Selexol™ is an AGR process employing physical absorption; solvents remove CO_2, H_2S, COS and mercaptans from Syngas streams[17]. The operations parameters and process description is detailed by Im, Roh, Kim, Eom & Lee (2015)[18] and it was being done in Unisim Design® using the DBR Amine Package as fluid package; which reproduces with good accuracy the dynamic and physics phenomena inside the absorption tower.Finally, a sensitivity analysis was implemented to evaluate the final conversion of CO to H_2O as a function of reaction temperature (between 230 to 300ºC).

Results and Discussion

EPFB pretreatment and gasification

For EPFB pretreatment, EPFB was dried and biomass was milled until 0.3 mm to increasing the heat transfer area and Syngas production efficiency. Gasifier selected to convert solid biomass to gaseous Syngas was a entrained-flow model over circulating fluidized bed biomass gasifier model – reported like one of the most efficient for several authors[19,20, 21]which can present some technical limitations due to high amounts of silicon and other metals present in ash, and the bed material, constituted mainly for sand which melting point is close to operation temperature; creating dynamic problems for sinterization, gasificant agent implemented was a mixture composed by steam and pure oxygen. In other studies Thermal efficiency and reaction yield of entrained-flow gasifier was high (99.5% and 95.8% respectively) and the tar yield was low. On the other hand, control over the gaseous components is easy in this model of gasifier; other kinds of biomass can be transformed; and no catalyst is required[22]. Hydrogen flowrate was estimated in 764.5 kg/h from an EPFB flow rate of 18147 kg/h. In Table 2, flow rates for mainly gases present in Syngas through different stages are registered. In addition, it is observed that in Gas Cleaning/Conditioning stage, hydrogen concentration was reduced due to hydrogen solubility in the water which is use as solvent.

Table 2. Syngas composition in the outlet stream of mainly systems of the process (kmol/h)

Component	Gasifier	Gas Cleaning/Conditioning	HT/LT Shift	Purification
H_2	380.7	370	505.47	498.72
CH_4	84.6	81.1545	81.1545	41.57
CO	141	137	1.53	1.24
CO_2	493.51	159	294.53	0.0903

Oxygen flow rate required to gasify EPFB is 7896.29 kg/h and is obtained from the High and Low pressure columns system present in ASU which are represented in stage 1 of Figure 2. ASU was simulated as a system of compressors with intercooling which rise the air pressure from 1 to 5 atm to operate the High Pressure Tower and a RadFrac module with 110 K of temperature and 44 equilibrium stages (stage 2). Conditions in LP distillation column were stablished in order to reach an outlet oxygen stream with a 98% of purity, being 80 K for temperature and 1.5 atm for pressure. Nitrogen obtained as sub-product can be used as a cooling service, a gas cleaner or like a raw material to synthetize other substances, as ammonia.

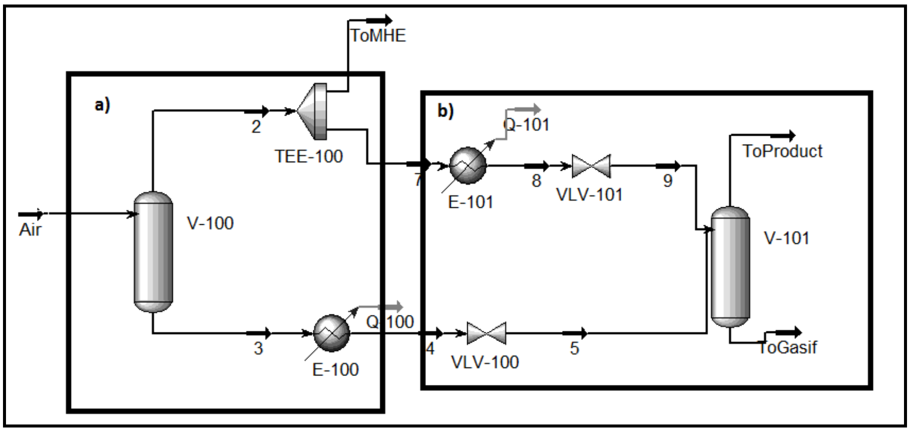

Figure 2. HP (High pressure) and LP (Low pressure) column system of ASU cryogenic air distillation unit.

Heat Recovery and Cleaning

Heat recovery and cleaning processes are illustrated in stage a) of Figure 3. First, Heat recovery stage was simulatedusing UniSim Design, where the gas is cooled until 60°C. During this process, water flow rate of 15185.14 kg/h at 25°C was used as service stream, leaving the system at 143°C as a stream in vapour phase which can be used as a heating service or to generate energy through a turbine.

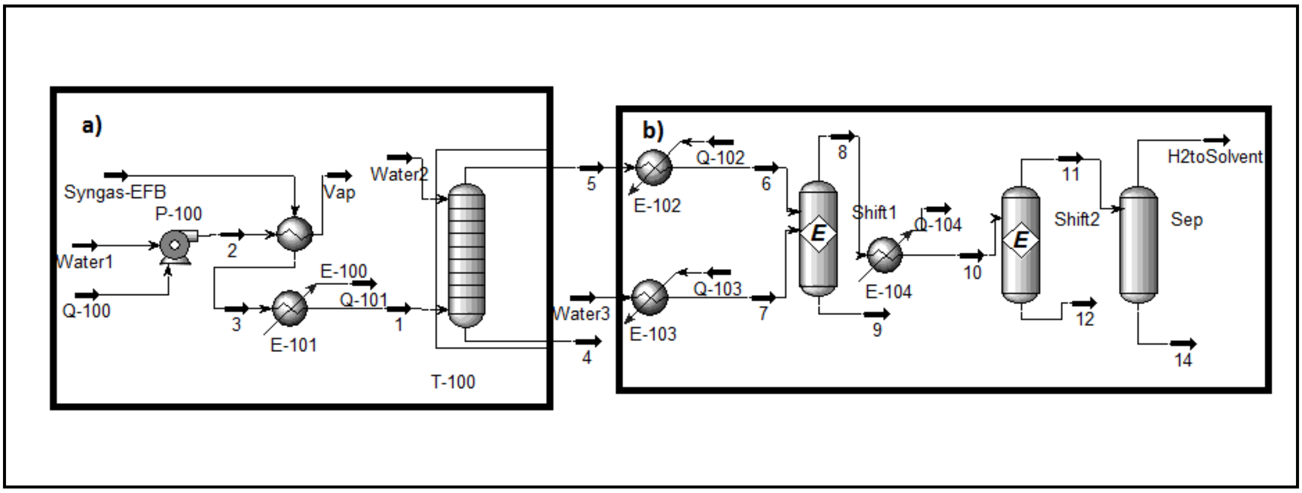

Figure 3. Heat recovery, gas cleaning, LTS (*Low Temperature Shift)* reactors, HTS (*High Temperature Shift)* and decanter stages.

Then, Syngas was cooled until 10°C to get into scrubbing unit, where a water flow of 390613 kg/h was used to dissolve the CO_2 present in Syngas before the HTS stage. This unit was modeled as a Flash 2 module at 60 atm of pressure with 9 equilibrium stages. In this process, 14715.7 kg/h of CO_2 were removed from Syngas, obtaining an outlet flow of Syngas 12873.6 kg/h. After this process, Syngas was heated until HTS reactor temperature.

Shift Reaction

Temperature Shift Reactors System is illustrated in stage b) of figure 3. In HTS reactor, the conditions were adjusted at 58 atm and 370°C. HTS reaction is not very sensitive to pressure changes as temperature, catalyst type and $[H_2O]/[CO]$ ratios. Due to this dependence to the variables mentioned before, a sensitivity analysis was carried out. In this analysis, hydrogen outlet flow of the HTS reactor was analyzed in base of the changes in $[H_2O]/[CO]$ ratio and temperature values. According to Figure 4, with a $[H_2O]/[CO]$ of 8 the maximum yield is reached, which means that increments in flow rate of steam which gets into HTS reactor are traduced in more hydrogen in outlet stream, but the difference between the flow rate reached with a $[H_2O]/[CO]$ ratio of 8 and a $[H_2O]/[CO]$ ratio of 6 is few, which means that a high yield can be reached with less water. On the other hand, in the lowest temperature of the range the maximum hydrogen yield in the reaction is reached; and this means that at lower temperatures the yield can be higher. However, the commercial catalyst for this reaction is activated at higher temperatures; for this reason, operation conditions related with temperature are subjects to this parameter. In LTS reactor the temperature depends of the Dew Point temperature of the water present in the Syngas at the pressure of the system[23]. HTS and LTS reactors were modeled as equilibrium reactors. After shift reaction stage, Syngas gets into a flash distillation drum, in order to separate water of the gas product. This device was simulated as a Flash 2 drum at 35°C and 36 atm, obtaining a Syngas flow rate of 15,050 kg/h and a water flow rate of 28,532 kg/h.

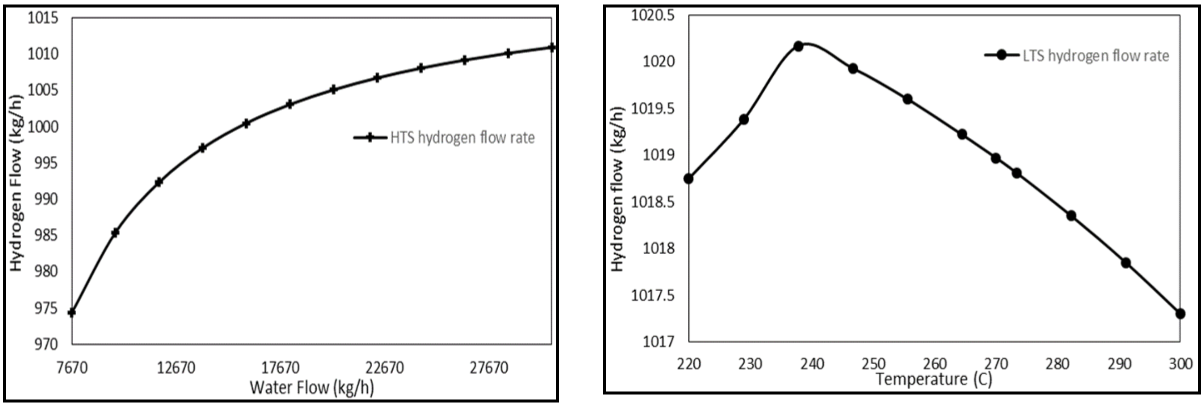

Figure 4: Effect of hydrogen flow rate in the outlet of HTS and LTS reactors.

Acid gas removal (AGR) process

For hydrogen flow purification, a physic absorption process was implemented. In other biomass to ammonia process[14], Rectisol™ was implemented like the physical solvent to absorb the CO_2 from Syngas due to its cost is lower than Selexol™ cost[24].

Characteristic of equipment for reaching low temperatures (around -10ºC) needed in the AGR process with methanol increases the fixed and operating cost of the process. On other hand, devices for Selexol™ process can be made of carbon steel due it is non-corrosive. Selexol flow rate to purify the hydrogen stream was 974,850 kg/h and operating conditions were 10°C and 36.2 atm. Selexol™ and a stream of 91.4 of hydrogen dragged by the solvent during the absorption process are recuperated through Flash drums, where a stream of 9156.8 kg/h of CO_2 can be used as raw material in the process to synthetize Urea (stage 2 of Figure 5). Hydrogen and Selexol™ recuperated were recycled to the absorption tower in order to increment the process efficiency and reducing the operating cost related with fresh solvent.

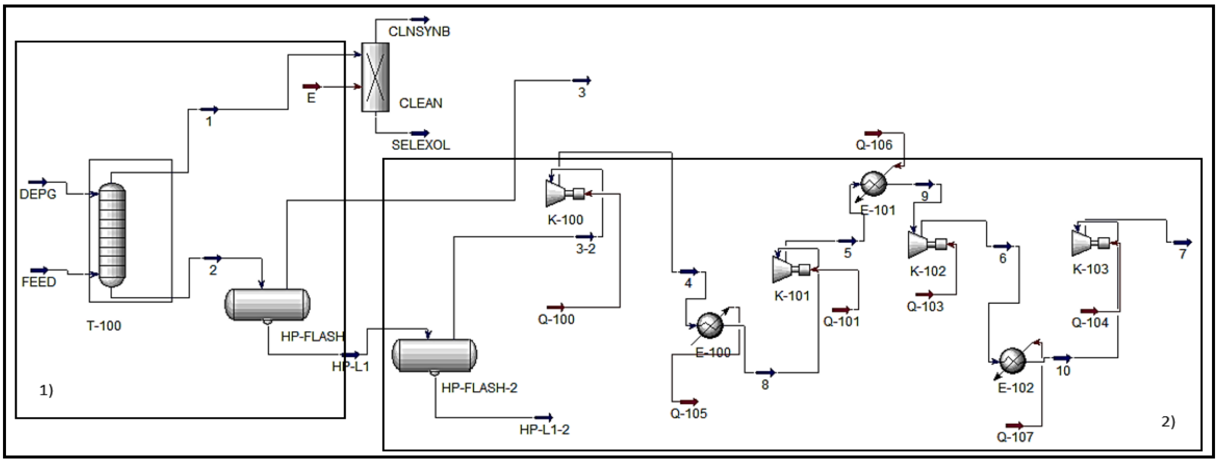

Figure 5. Syngas purification process using Selexol™ as solvent.

Conclusions

In this study, can be produced 3989.76 t/yr of hydrogen from Empty Palm Oil Bunches. Hydrogen production was favored with drying of feedstock and a transient heat flow rate into the gasifier, hydrogen purification efficiency increased using Selexol instead of Rectisol owing to its boiling point allows a CO_2 separation with a pressure change without the need of desorption stage. Other advantage of the process is that Sulphur separation unit is not needed owing to its low concentration in EPFB. This process is very demanding in services as water, power and heat. Some devices as gasifier and ASU unit can be integrated thermally in order to save money in operating costs.

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