Environmental Assessment of a Biorefinery:

Case Study of a Purification Stage in

Biomass Gasification

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Abstract

This work presents an environmental assessment of a multi-feedstock biorefinery, which has a special purification stage in the gasification process. In that process,

syngas is obtained with high yield of CO, and a water gas shift reaction to increase the yield of H_2 is necessary. This reaction produces CO_2, which has to be separated from H_2. The biorefinery was simulated in ASPEN PLUS software. The physical and chemical properties of the streams were predicted using the National Renewable Energy Laboratory's (NREL) database. Residues of rice, corn, banana, and cocoa were used as raw materials. The environmental assessment was developed in the WAR GUI software based in the simulations results. Two cases were evaluated for purification of the output stream coming from water gas shift reaction. As results, the ethanolamine impact in the Photo-Chemical Oxidation Potential (PCOP) category for the case A was 300 PEI/kg of product and the Potential Environmental Impacts (PEI) generation for case B was 2.55 per kilogram of product.

Keywords: Environmental assessment, hydrogen, gasification, purification

1 Introduction

In the recent decades, interest in the conservation of nature's resources has increased, and process sustainability criteria have been used in almost every industry. Associated with the availability of resources, there are concerns about the increase in global energy demand, which has led to an increase in greenhouse gas (GHG) emissions [7]. In this scenario, the biofuels industry has emerged as an important alternative not only to reduce energy demand but as a way to produce a variety of chemical goods.

The energy production from biomass has grown 23% from 1993 to 2011, and it is projected for 2020 that the production will be 1,323 Mtoe (Million tonnes of oil equivalent) [13]. Hydrogen is considered a clean fuel, which does not emit carbon dioxide or GHG's in combustion process and can be used in fuel cells for electricity generation. In addition, hydrogen has an energy efficiency of 122 kJ/g, which is 2.75 times higher compared with hydrocarbons [2]. There are conventional methods of production, which include: Steam Reforming of Methane, Non-catalytic Partial Oxidation of Fossil Fuels, and Self-thermal Reforming involving the combination of the two processes mentioned previously. The main drawback in the use of these methods lies in the temperature and energy requirements, so in the last years the interest in the biohydrogen production has increased [8].

Biomass gasification is a thermodynamic process related to incomplete combustion for the carbon monoxide, hydrogen, and methane traces [5]. This process is carried out in a reactor called Gasifier, which is usually operated at 1,000 °C. In general, the products of the complete combustion of biomass are substances that contain nitrogen, water vapor, carbon dioxide, among others.
In the gasification, syngas can be obtained as a final product, mainly composed of

hydrogen and carbon monoxide. From these processes hydrogen can be obtained at high concentrations through a process called Water Gas Shift, which is an equilibrium reaction, where carbon monoxide and water are combined to form hydrogen and carbon dioxide [11], as follows:

$$CO + H_2O \leftrightarrow H_2 + CO_2 \tag{1}$$

The system leaves a mixture with high carbon dioxide content, which needs to be separated to obtain the desired product at the highest possible concentration. There are several methods to separate carbon dioxide from hydrogen: gas absorption, filtration, membranes, and so forth [14].

The environmental assessment is used to evaluate the performance of several alternatives.

In this work is developed an environmental assessment of a multi-feedstock biorefinery for different purification processes applied in the separation of carbon dioxide from hydrogen, coming from the gasification process. The assessment was made using data obtained from ASPEN PLUS simulations for different configurations of the purification stage. The environmental evaluation was carried out through WAR GUI software.

2 Biorefinery Simulation

The biorefinery was simulated to process 1,076,192 t/yr residues of cassava, rice, corn, banana, and cocoa since is the amount reported by the Ministry of Agriculture and Rural Development for 2014.

The gasification process was simulated to process 478,257 t/yr of corn stover, rice straw, rachis of banana, and cocoa shell, according to a base case obtained from the solution of an optimization model applied to a biorefinery design. The raw material is mixed and sent to a dryer to remove the moisture until reaching humidity below to 10% [9]. Subsequently, the stream is sent to the gasifier, which operated at 750°C, under atmospheric pressure, when hydrogen as main product and carbon monoxide, carbon dioxide, and methane, among others are obtained. The gas phase and solid by-products of the reaction are separated in cyclones. The gaseous stream is sent to cooling to reach a temperature of 15°C, allowing the condensation of an important amount of water. To remove the carbon dioxide present in the gas mixture, the stream is sent to an injector, where water is used as the absorbing medium, the stream is compressed at 6 bar, and sent to a separator to withdraw water along the dissolved carbon dioxide (Fig. 1 shows the diagram process and simulation flowsheet for the biomass gasification plant) [1].
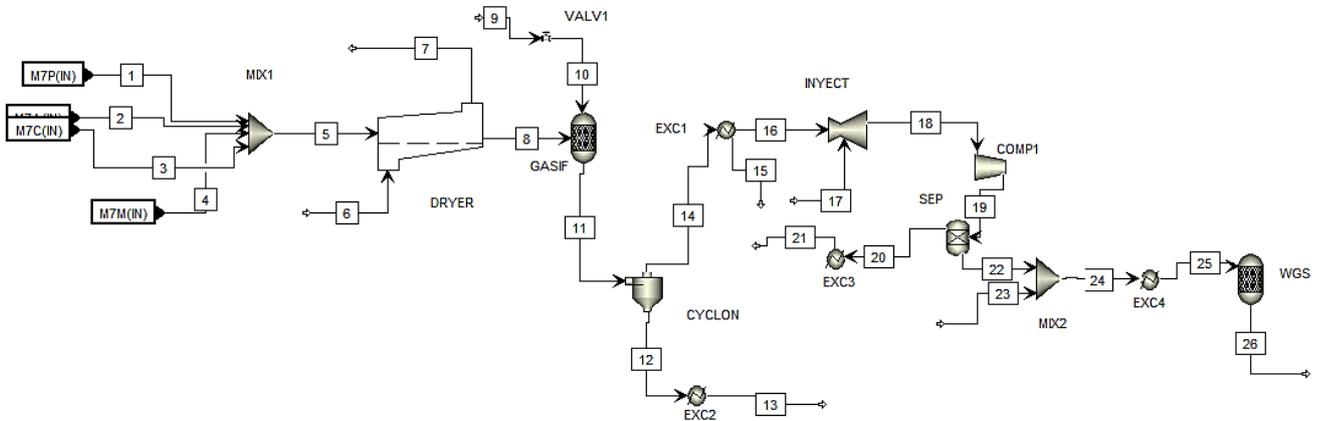
Figure 1. Gasification base simulation. MIX1: Mixing unit 1, DRYER: Dryer unit, GASIF: Gasification reactor, CYCLON: Cyclone separation unit, EXC1: Heat exchanger unit 1, EXC2: Heat exchanger unit 2, EXC3: Heat exchanger unit 3, INYECT: Injection unit, COMP1: Compression unit, SEP: CO_2 separation unit, MIX2: Mixing unit 2, EXC4: Heat exchanger unit 4, WGS: Water gas shift reactor.

2.1 Purification Stage: Case A

To increase the concentration of bio-hydrogen, a WGS reaction is used, (Eq. 1). The equilibrium is favorable to the products when the system operates at 205°C and 32 atm. In the WGS reaction carbon dioxide is generated as a byproduct with hydrogen as main product, therefore it is necessary to develop a purification stage that allows the capture of carbon dioxide in order to get a final product with high purity. There are different methods applied to gas separation. For case A, the purification stage was simulated according to gas absorption with monoethanolamine (MEA), which allows the purification of the syngas and reach up to a 97 %v/v purity of hydrogen [3]. Figure 2 shows the purification stage simulation for case A.
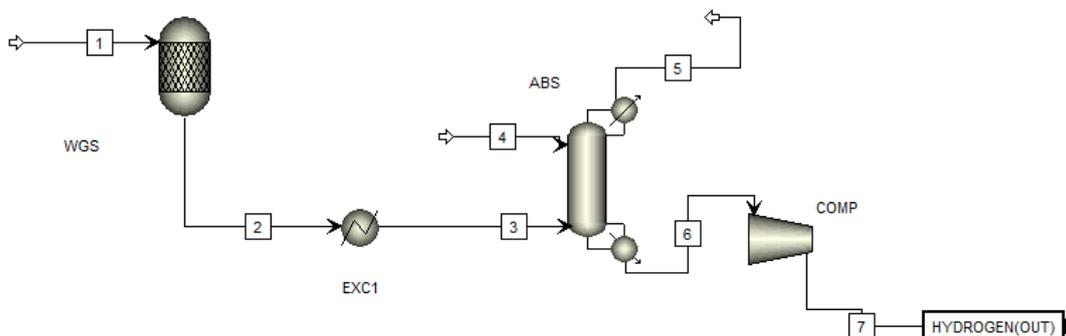

Figure 2. Case A: process flowsheet. WGS: Water gas shift unit, EXC1: Heat exchanger, ABS: Absorption unit, COMP: Hydrogen compression unit.

2.2 Purification Stage: Case B

According to the description of case A, the hydrogen purification process involves the realization of the WGS reaction. Due to the complexity of the separation of carbon dioxide from the reaction mixture, a membrane/filter technique is applied to achieve a concentration of 99% of H_2 [12]. Figure 3 shows the purification stage simulation for case B.
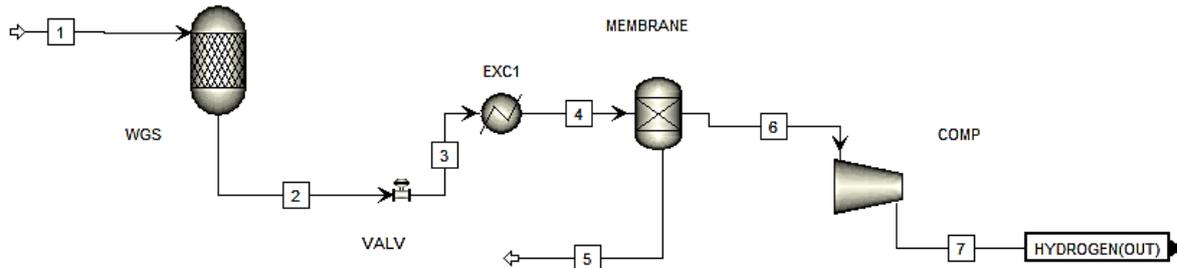

Figure 3. Case B process flowsheet. WGS: Water gas shift unit, VALV: Pressure regulator, MEMBRANE: Membrane/filter unit, COMP: Hydrogen compression unit.

3 Environmental Assessment

To estimate the PEI of the biorefinery operations WAR GUI software developed by the US Environmental Protection Agency (EPA) was used. WAR GUI evaluates process through eight categories: human toxicity by ingestion (HTPI), human toxicity by dermal exposure or inhalation (HTPE), aquatic toxicity potential (ATP), global warming (GWP), ozone depletion (ODP), photochemical oxidation potential (PCOP), and acidification potential (AP).

4 Results and Discussion

The environmental assessment was developed for both cases using WAR GUI. PEI for an amount of mass or energy can be defined as the effect that these flows can cause in the environment if they are arbitrarily discharged [6]. In Fig. 4 we can see the environmental assessment to case A:
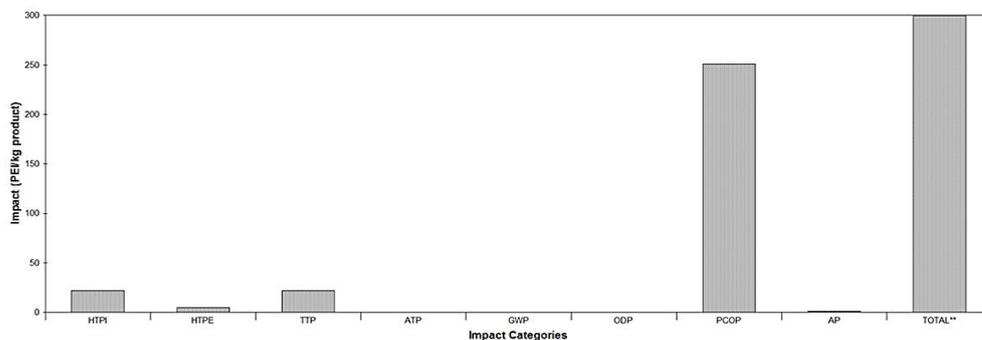

Figure 4. PEI/kg for case A

With the emissions of fossil sources and compounds such as ethane, ethylene, acetone or formaldehyde, the greatest effect is related to damage to human health due to respiratory problems, eye irritation, and loss to some materials [10]. The impact of PCOP category, obtaining approximately 250 PEI/kg product, was increased due to the use of ethanolamine in the process of separation of CO_2 in H_2 purification, a compound which by its molecular structure is considered to have a photochemical degradation potential 2.19 times greater than the reference value, which is based on the emissions of ethylene [4].

For case B a modification was made in the design and simulation in the CO_2 capture stage, in which instead of a CO_2 absorption with amine, it was used a filter/membrane with high purity hydrogen production. For this case, the hydrogen production was slightly different, which went from 1,627.2 kg/h for case A, to 1,622.8 kg/h for case B. Therefore, to evaluate the case B the energy and mass balances were adjusted in WAR GUI and the program was ran again.
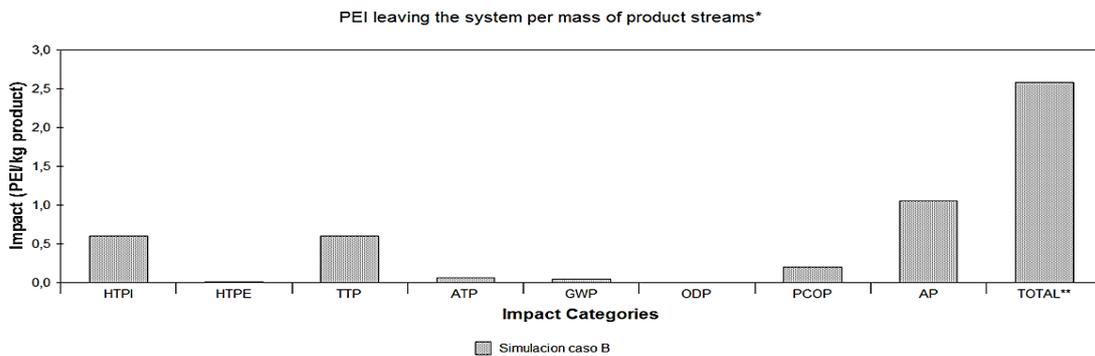

Figure 5. PEI/kg for case B

Figure 5 shows the PEI/kg of product of the modified case B, for each kilogram of product(s) generated in the operation there is a potential environmental impact of 2.55, which implies an important reduction compared to the simulated case A. Another important aspect is the reduction of impact in the PCOP category, which was reduced to 0.198 PEI/kg of product, due to the removal of ethanolamine in the purification stage.
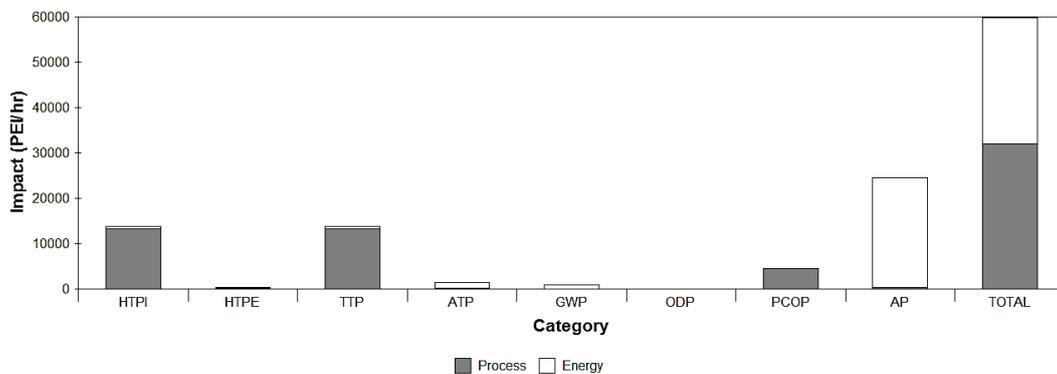

Figure 6. Contribution by mass and energy in PEI case B

As for a global analysis, for case B the biorefinery would generate about 5.98×10^4 PEI/h, of which 2.78×10^4 PEI/h are related to the potential impacts due to the energy consumption from biorefinery operations by the use of fossil fuel. Figure 3 shows the environmental categories evaluated and the contributions in the impacts by both mass flow and the use of fuels for energy supply.

4 Conclusions

In this study, a biorefinery design was evaluated for two cases of different alternatives in the purification stage of biomass gasification process. The results shows for case A, the use of the ethanolamine increases PEI generation, specifically photochemical degradation potential is the most impacted categories, resulting in 300 PEI generated per kilogram of product. For the case B, a modification was made at this stage of the process with the use of membrane/filters to avoid potential impact for ethanolamine, the results shows that was obtained an important reduction in the potential environment impacts for this case, obtaining 2.55 PEI per kilogram of product, for that reason, case B is proposed as the basis of design for purification stage in the gasification process.
Finally biorefinery based on case B, generates roughly 5.98×10^4 PEI/h, of which 46.48% refers to the impacts associated with the energy supply by use of fossil sources. This reflects that almost half of the impacts were generated from for the use of sources as gasoline, coal or gas. Avoiding this kind of substances could improve the environmental performance of the biorefinery.

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