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Abstract. Bioethanol is a liquid fuel that can be produced from various raw materials. The first generation of bioethanol which are starch and sugar has begun to decline as these materials are considered to be the food sources for human as well as animals. However, the rise of production of bioethanol from the second generation which are the lignocellulosic materials has been proven to give a lot of benefits to mankind instead. Various technologies were studied in order to design an optimal processing route for bioethanol production from lignocellulosic biomass. A superstructure on the available process technologies which include the three main technologies, the pretreatment, sugar conversion, separation and purification was first developed before screening it down to a final superstructure. All of the data have been used in this study were collected from open literature and followed by the selection and development of the models required in order to solve the generic models and problems by using an optimization software, the Generic Algebraic Modelling System (GAMS). The optimization results indicate that the optimal processing route in producing bioethanol from lignocellulosic biomass include the technologies of steam explosion, dilute acid followed by fermentation, beer and dehydration of ethanol on zeolite for each process interval with maximum yield of 2238.4 kg/h.

1. Introduction

As the global energy demand keep increasing, the shortage of energy will be a global threat to mankind. The presence of bioethanol can be considered as an important renewable fuel to replace fossil fuels and it is also the most used liquid biofuel in the world. Along with the growth of modernization and industrialization, the demand of bioethanol also has shoot up. In fact, ethanol has long been considered as a suitable alternative to fossil fuels either as a sole fuel in cars with dedicated engines or as an additive in fuel blends with no engine modification requirement when mixed up to 30% [1]. Over the years, the ethanol produced from biomass also has become an increasingly popular alternative to gasoline [2]. As stated by Demirbas [3], unlike gasoline, ethanol is an oxygenated fuel that contains 35% oxygen, which reduces particulate and NO_x emissions from combustion.

Bioethanol can be produced from various raw materials. Sugar and starch based materials such as sugarcane and grains are two groups of raw materials usually used as the main resources for ethanol production while the second group is lignocellulosic materials representing the most viable option for production of ethanol [1]. Due to the agro-ecological conditions, North American and European are the countries that mainly produced bioethanol from starchy materials. Meanwhile, in Brazil, sugarcane is the main feedstock used for bioethanol production. However, in the subsequent years, sugar and starch based materials are not preferable anymore in producing bioethanol as these materials are considered to

be the source of food. This has led researchers to find another alternative, which are the lignocellulosic materials that are much more promising as feedstock taking into account the viability as well as the cost needed to utilize the feedstock. In many developing countries, food-related feedstock is preferably replaced by non-food raw materials such as sweet sorghum or cassava [4]. Other lignocellulosic materials include agricultural residues or crops such as sugarcane bagasse, corn stover and rice husks.

In general, lignocellulosic biomass can be converted into ethanol through two types of conversion, namely biochemical and thermochemical. Biochemical conversion of biomass involves the technologies of pretreatment followed by hydrolysis to convert the feedstock to simple sugars before these sugars are being fermented to bioethanol. Meanwhile, thermochemical conversion of biomass includes biomass gasification to syngas which are mainly CO and H_2 that can be further synthesized into a wide range of different fuels and chemicals under different catalysts and operating conditions [5]. However, with abundance of technologies available to produce ethanol, the concern of finding the best process route is very significant to produce a high quality fuel grade ethanol. Therefore, in this study, various process technologies available in biochemical conversion were studied in order to synthesis and design an optimal processing route of producing bioethanol from corn stover feedstock through an optimization software, GAMS [6].

2. Materials and Method

2.1. Construction of Systematic Approach for Synthesis of Bioethanol Production
The systematic approach comprises of five main steps and the flow chart of the overall process is shown in figure 1 where the computer-aided support tools are integrated with the workflow in order to deal with the complexity of the synthesis problem. Each step presented in the framework is explained in the following section.
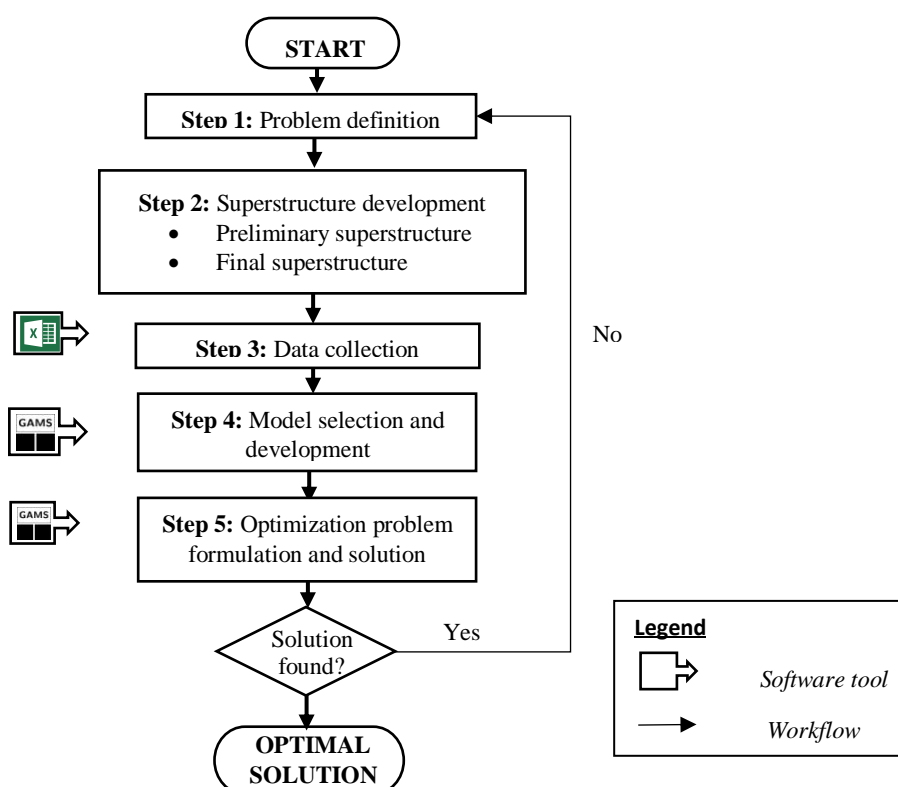
 Figure 1. A systematic approach for synthesis of bioethanol production from lignocellulosic biomass.
2.1.1. Step 1: Problem Definition. The objective of the optimization problem is to find the optimal process topology for producing bioethanol through biochemical route. Various alternatives and technologies were listed before finalizing the best process to be used in the production of bioethanol.

2.1.2. Step 2: Superstructure Development. In this section, the superstructure was developed by listing all the available routes exist in producing bioethanol. The pretreatment methods, sugar conversion technologies as well as separation and purification methods were the factors to be considered in the selection of the process technologies and superstructure development. A prior screening process should be performed for the identification of the technologies to be located in the superstructure and the interconnections between the technological alternatives which defined by the experts. If the data and information for feasible technology was not available, the technology was discarded from the superstructure representation. Each processing step in the superstructure consists of one or more intervals that represented a block. The generic block incorporates generic models to represent alternative processing steps and a simple block used to represent the activities of processing technologies [7-8]. Depending on the step and process technology employed, process intervals can be characterized by a simple process flowsheets of different structure or represented as a series of unit operations which consist of flow mixing, utility dosage, reaction, waste separation, product separation and flow division as shown in figure 2. Table 1 summarizes the available technologies for each conversion step involves biochemical processing routes.
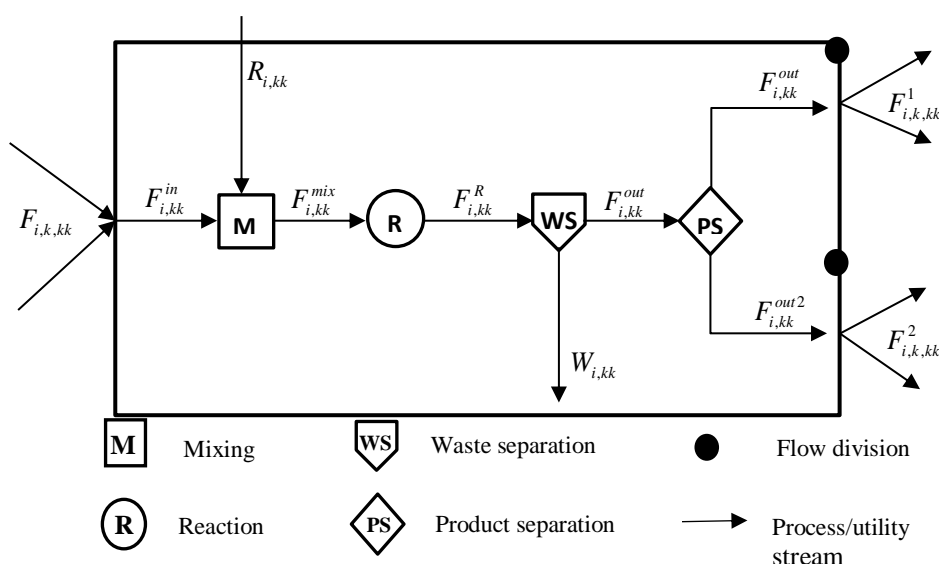
Figure 2. Schematic representation of the generic process interval.

Table 1. Available technologies for conversion of corn stover.

Conversion step	Process Technology	References
Pretreatment	Steam Explosion	[9]
	Controlled pH	
	Dilute Acid	
	Ammonia Fiber Explosion	
	Ammonia Recycling Percolation	
	Lime	
Hydrolysis	Dilute Acid	[3]
Fermentation	Concentrated Acid	
Separation	Beer column	[10]
Purification	Dehydration of ethanol on zeolite (Rect+Zeo)	[11]
	Dehydration of ethanol on glycerol (Glycer)	[12]
	Dehydration of ethanol on ethylene (Ethyl)	[13]
	Dehydration of ethanol on ionic liquids (ILs)	[14]
	Dehydration of ethanol on silica (Rect+Sil)	[15]

2.1.3. Step 3: Data Collection. For data collection, significant data and information for each possible technology were collected from different resources. All of these data and information then were stored and saved in Microsoft Excel as a database. All relevant information on raw materials as well as the process intervals were also collected. The data and parameters required for the generic data for the intervals include reaction conversion, utility consumption, and split fraction, which are identified by input-output information. The data were obtained from open literature including experimental and pilot plant studies.

2.1.4. Step 4: Model Selection and Development. After defining superstructure and collecting related data, the next task is the selection and development of models describing each of the element of the superstructure as well as the models required for the calculation of the selected objective function (i.e maximum yield) and the performance criteria. In this case, objective function is to obtain maximum product yield as given in equation (1).

$$Yield = \sum_{i,kk} F_{i,kk}^{out} \tag{1}$$

The process models used in this paper are adapted from [7] as presented in the Appendix. Sets of generic equations representing a sequence of processing tasks, which are mixing, reaction, waste removal and product separation, as well as utility consumption were modelled for each interval in the superstructure. Multiple inlets and outlets from the interval were allowed, including recycle streams from downstream intervals and bypasses.

2.1.5. Step 5: Optimization Problem Formulation and Solution. In this last step, the equations, constraint and logical are generally expressed as Mixed Integer Linear Programming (MILP) problem. The optimization problem was solved by employing solver from an optimization software, GAMS. The inputs to the solver were the generic model and an input file with all the necessary problem data such as the raw materials, feed composition, component and model parameters. The outputs from the optimization were the optimal values of the objective function, the corresponding optimization variables and all other process variables.

3. Results and Discussions
The conversion of lignocellulosic biomass to bioethanol in the biochemical conversion platform may go through multiple routes with different available technologies that have different economic performances. In this case study, it is desired to produce 99.5% pure bioethanol from corn stover. The feedstock composition is presented in table 2. It is assumed that the hydrolytic enzymes were purchased from commercial suppliers.

Table 2. The feed composition.

Component	% Dry Basis
Lignin	16
Xylan	16
Arabinan	2
Galactan	1
Cellulose	31
Water	24
Ash	10

The objective of the optimization problem is to find the optimal process topology for producing bioethanol through biochemical route that gives the highest bioethanol yield. The superstructure was

constructed based on the available of data and information for all viable options of process topology for the bioethanol production from corn stover as shown in figure 3. As can be seen in figure 3, the bioethanol processing network superstructure are composed of 1 raw material (corn stover) 17 process intervals represent different technologies structured in 5 processing steps and 1 product (bioethanol). Also, 34 components and 3 utilities are considered in this problem.
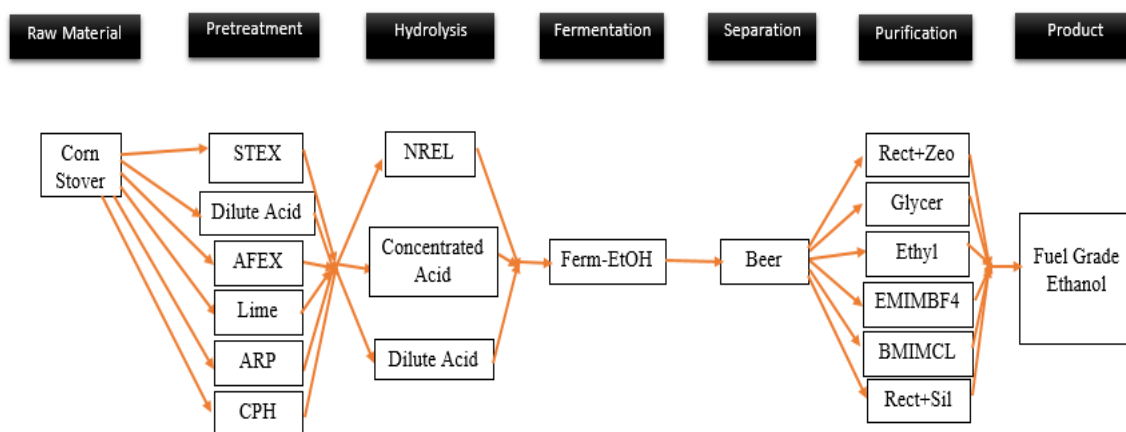
Figure 3. Superstructure of available raw materials and processing routes.

The optimization problem was formulated as MILP and solved using CPLEX/GAMS using GAMS version 23.9.5 [6] to identify an optimal processing route. The case study was performed using a standard computer, equipped with 2.40 GHz Intel (R) Core™ i5-6200U. The superstructure features 987,938 number of variables, and 1,644,456 number of equations as presented in table 3.

Table 3. Statistics optimization problem for bioethanol production process

Number of variables	987,938
Number of equations	1,644,456
Problem type	MILP
Solver	GAMS/CPLEX
Execution time	0.249 seconds

Results for the selected process topology are given in table 4. It is found that steam explosion (STEX) has been selected for the pretreatment step. In STEX process, high-pressure saturated steam is added in which it initiates the hydrolysis reaction. Pressure is then suddenly reduced, exposing the feedstock to an explosive decompression which opens the biomass structure, thus, increasing the accessibility of the enzyme [16]. Meanwhile, for hydrolysis, the results on GAMS showed that the optimized process technology was dilute acid. According to Alvira et al. [17], this method does not only solubilize the hemicellulose which is mainly xylan, but it also converts the solubilized hemicellulose to fermentable sugars. The process route then continued with fermentation and separation before being purified to fuel grade ethanol. In this last step, the optimized route based on GAMS was rectification with zeolite. Abdeen et al. [11] stated that zeolites are proven to be efficient in removing the water from ethanol-water azeotrope due to their small pore size of less than 0.3nm which allows only water to adsorb to the inner large surface area of zeolite. Based on the optimization results obtained from GAMS, the maximum yield that can be achieved for the selected process technologies is 2238.4 kg/h. The optimal processing route is shown in figure 4.

Table 4. Mass flow for the selected process technologies.

Process Technology	Mass Flow (kg/hr)
STEX	5175.4
DILA	5175.4
FERM-ETOH	6790.0
FILTR	8090.0
BEER	6896.1
RECT+ZEO	2314.8
FEUL GR ETOH	2238.8
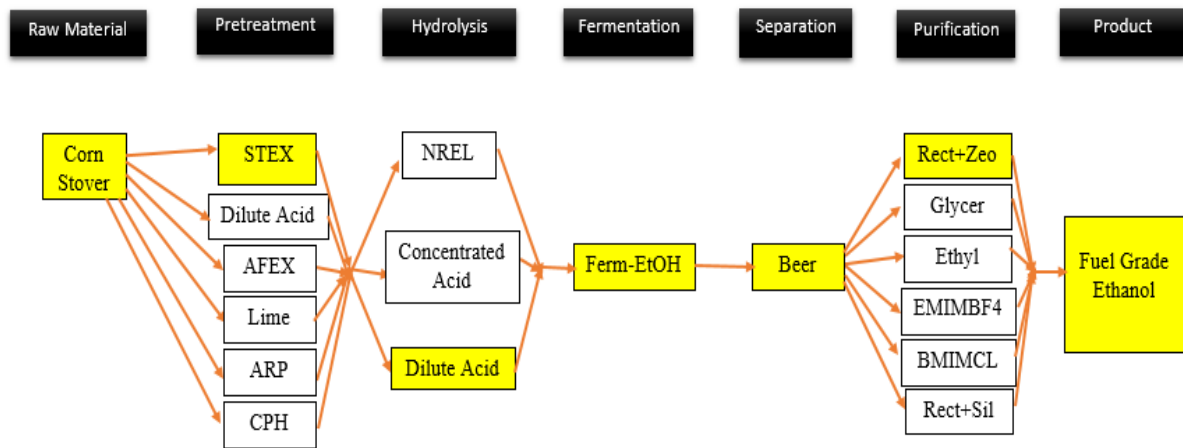
Figure4. An optimal processing route for bioethanol production from corn stover –highlighted the selected process technologies.

4. Conclusion

Based on the results obtained, the selected processing route for pretreatment, hydrolysis, separation and purification process interval were steam explosion, dilute acid followed by fermentation, beer and dehydration of ethanol on zeolite respectively with maximum yield of 2238.4 kg/h. The superstructure-based optimization methodology has been shown to be a useful decision support tool for early stage synthesis and design of bioethanol production from lignocellulosic biomass by screening a number of process technologies.

Appendix

$$F_{i,kk}^{mix} = F_{i,kk}^{in} + \sigma_{i,kk} CU_{i,kk} \tag{A.1}$$

$$CU_{i,kk} = \sum_{ii} (\mu_{i,ii,kk} \cdot F_{i,kk}^{in}) \tag{A.2}$$

$$F_{i,kk}^{R} = F_{i,kk}^{mix} + \sum_{rr,react} (\gamma_{i,kk,rr} \cdot \theta_{react,kk,rr} \cdot F_{react,kk}^{mix} \cdot \frac{MW_i}{MW_{react}}) \tag{A.3}$$

$$W_{i,kk} = F_{i,kk}^{R} \cdot SW_{i,kk} \tag{A.4}$$

$$F_{i,kk}^{out} = F_{i,kk}^{R} \cdot (1 - SW_{i,kk}) \tag{A.5}$$

$$F_{i,kk}^{out1} = F_{i,kk}^{out} \cdot SPr_{i,kk} \tag{A.6}$$

$$F_{i,kk}^{out2} = F_{i,kk}^{out} \cdot (1 - SPr_{i,kk}) \tag{A.7}$$

$$F_{i,kk}^{out1} = \sum_{kk} F_{i,k,kk}^{1} \tag{A.8}$$

$$F_{i,kk}^{out2} = \sum_{kk} F_{i,k,kk}^{2} \tag{A.9}$$

$$F_{i,kk}^{in} = \sum_{k} (F_{i,k,kk}^{1} + F_{i,k,kk}^{2}) \tag{A.10}$$

$$F_{i,k,kk}^{1} = F_{i,kk}^{out1} \cdot \xi_{k,kk}^{P} \cdot SM1_{k,kk} \tag{A.11}$$

$$F_{i,k,kk}^{2} = F_{i,kk}^{out2} \cdot \xi_{k,kk}^{S} \cdot SM2_{k,kk} \tag{A.12}$$

$$F_{i,kk}^{out} = \emptyset_{i,kk} \cdot y_{kk} \tag{A.13}$$

$$0 \leq f_{i,kk} \leq y_{kk} \cdot M \tag{A.14}$$

$$\sum_{kk} y_{kk} \leq 1 \tag{A.15}$$

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