Potential of lignocellulosic biomass for jet fuel precursor production through catalytic transformation technologies

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Abstract

This work presents a new perspective for the experimental conversion of sugarcane bagasse (SCB), coffee cut-stems (CCS) and fique bagasse (FB) to obtain precursors of liquid alkanes range jet fuel (4-(2-furyl)-3-buten-2-one or FA) using as catalyst MgO-ZrO_2. The yields obtained in the experimental procedure are used as starting point of the simulation procedure in order to evaluate the economic and environmental performance of the process. The experimental procedure includes three stages: i) acid hydrolysis, ii) dehydration reaction and iii) aldol-condensation reaction. Two operation conditions for acid hydrolysis are selected and the performance of each condition is evaluated in the subsequent stages. High Performance Liquid Chromatography (HPLC) is used in the sugars and furfural determination in stages i) and ii). Besides, Gas Chromatography–Mass Spectrometry (GC-MS) is used in stage iii) for the FA determination. The experimental results show that the best yields are for SCB, in the acid hydrolysis are obtained 0.81 and 0.6 grams of xylose per grams of hemicellulose for condition 1 and 2 respectively. In dehydration reaction CCS shows a good performance for condition 1 and 2 obtaining 0.063 and 0.067 grams of furfural per gram of xylose respectively. In aldol-condensation reaction for the condition 1, a furfural conversion of 96.5% for CCS is obtained. In the simulation results, CCS shows notable data, a production cost of 5.57 USD per kilogram and a medium value of total potential environmental impact per kilogram of product, in comparison with others raw materials.

Keywords lignocellulosic biomass, jet fuel precursor, catalytic conversion.

1. Introduction

The uncertainty on oil reserves, oil prices as well as the climate change have become in important reasons to search new alternatives to produce valuable chemicals and fuels [1], [2]. In this sense, biomass appears as a source to produce environmentally friendly biofuels and biobased materials with promising substitution capacity of petrochemical sources. The International Energy Agency (IEA) estimates that total energy supply of primary energy jumped from 6,106 Mtoe (Million tonnes of oil equivalent) in 1973 to 13,371 Mtoe in 2012. The substantial demand of fuels considers an increase in the use and availability of energy sources [3].

Countries as Colombia, located in tropical regions have an important production of raw materials and specifically a large amount of biomass. Some of them are of first and second generation: First generation raw materials are designed to obtain multiple products of added value, while second generation feedstocks are generally residues obtained from the processing of first generation feedstocks. Both raw materials are excellent platforms for obtaining biofuels and bioenergy. Second generation feedstocks are considered promising and particularly attractive, and worldwide many efforts have been devoted to its conversion. Especially, the derivation of biofuel from the catalytic conversion of lignocellulosic biomass has become one of the trendiest research subjects in the world [4], [5].

Biofuels as ethanol and biodiesel are well known for its commercial competition, calorific properties and sustainable production. In the last years, the research in biofuels has considered a new outlook and has changed the research field of the production of fuels for the land industry to the aircraft industry. Studies report that jet fuels range alkanes could be obtained from lignocellulosic biomass by a novel route, wherein C5 sugar is firstly produced by hydrolysis of biomass and then converted into furfural by a dehydration step; further furfural reacts with acetone by an aldol condensation step to produce jet fuel precursors, followed by the generation of long chain alkanes ranging from C8 to C15 via dehydration/hydrogenation step. From this process, alkane products have cetane numbers, a measure of the ignition quality of diesel fuel, ranging from 63 to 97, whereas the overall cetane number for diesel is typically from 40 to 55. The high cetane numbers for these biomass-derived alkanes make them excellent blending agents to produce sulfur-free diesel fuel for transportation applications [6], [7].

The process to convert renewable biomass into liquid alkanes range jet fuel comprises a series of consecutive reactions using furfural as platform product. Furfural offers an important and rich source of derivatives that have potential use as biofuel components [5], [8], [9]. Furfural is exclusively produced from renewable biomass sources by acid-catalyzed dehydration of pentoses because there is no available synthetic route [10]. In the hydrolysis and dehydration stages, dilute acid is used as catalyst. This homogeneous catalyst is effective and decomposes easily the hemicellulosic fiber of biomass in sugars and furfural [11]. Aldol-condensation step to form C_8 to C_{15} alkane precursors is carried out using MgO-ZrO_2 as catalyst [7], [12]. This heterogeneous catalyst has high activity and selectivity, as well as excellent recyclability and hydrothermal stability. The large compounds from this series of reactions undergo hydrodeoxygenation reactions to produce final alkanes [7], [12], [13]. **Figure 1** indicates the essential features of the reaction pathways involved in the production of precursors jet fuel (C_8 to C_{15} alkane precursors) from biomass-derived furfural.

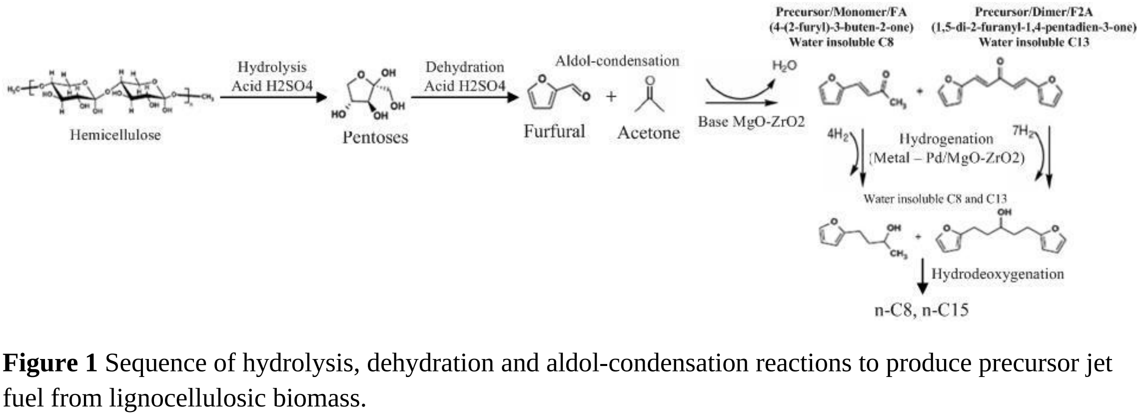

Figure 1 Sequence of hydrolysis, dehydration and aldol-condensation reactions to produce precursor jet fuel from lignocellulosic biomass.

The present study deals with the production of the main precursor (4-(2-furyl)-3-buten-2-one) to obtain alkanes range jet fuel from lignocellulosic biomass as sugarcane bagasse, coffee cut-stems and fique bagasse. Two operational conditions are assessed for each raw material. Details of the process reactions of hydrolysis, dehydration and aldol-condensation are indicated and the results obtained are compared.

The synthesis of the process scheme is carried out using simulation tools. The yields obtained in the experimental procedure are used as starting point in the simulation to evaluate the viability of the precursor production from SCB, CCS and FB. The good performance of aldol-condensation reaction according to disappearance percentage of furfural and appearance of precursor in qualitative terms is evaluated.

2. Materials and methods

2.1 Raw materials

Sugarcane bagasse (SCB) is obtained from a farm placed at Salamina town Caldas (5°26'02.1"N, 75°28'54.5"W), with altitude about 1,800 meters above sea level and has an average temperature of 22°C. Coffee cut-stems (CCS) is obtained from a farm placed at La Merced town Caldas (5°23'19.7"N, 75°32'46.1"W), with an altitude about 1,819 meters above sea level and has an average temperature of 19°C. Fique bagasse (FB) is obtained from a farm placed at Salamina town Caldas (5°22'49.2"N, 75°29'29.0"W), with an altitude about 1,800 meters above sea level and has an average temperature of 22°C. The chemical composition of the evaluated lignocellulosic biomass is shown in **Table 1** [14].

Table 1 Composition of the lignocellulosic biomass used in this work (% wt dry basis).

Component	SCB	CCS	FB
Cellulose	46.74	40.39	50.79
Hemicellulose	23.62	34.01	14.19
Lignin	19.71	10.13	12.47
Ash	1.13	1.27	21.84
Extractives	8.79	14.18	0.69

2.2 Experimental process description

Figure 2 shows the diagram description of the proposed experimental process. Jet fuel production can be described as a four stages process. A concise description is shown as follows.

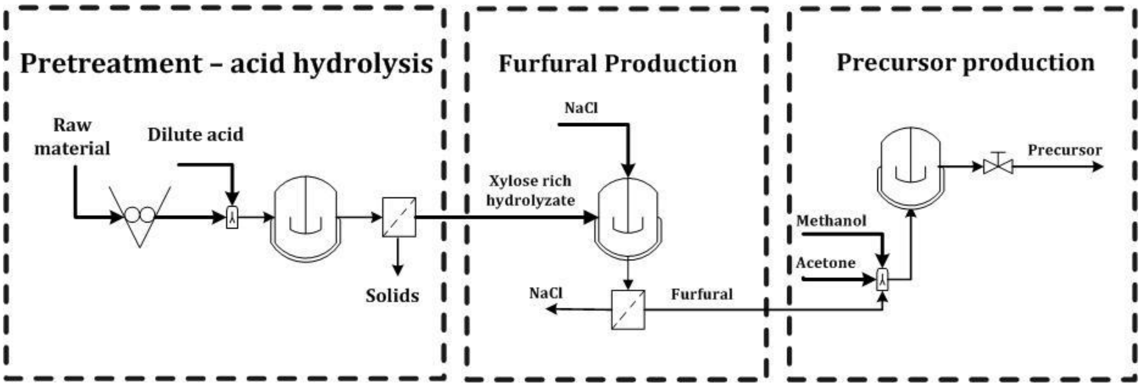

Figure 2 Flowsheet for process to obtain jet fuel precursor.

2.2.1 Dilute-acid pretreatment

Acid pretreatment of raw materials is carried out using two operation conditions: i) sulfuric acid solution (2 %v/v) at 110ºC [15] and ii) sulfuric acid solution (10% v/v) at 110ºC [16]. The solid to dilute-acid solution ratio is 1:10 (wt/wt) and reaction time is 5 h. The reaction time of the second condition is 30 min. After pretreatment, the solid fractions and liquor are separated by filtration. Rich-sugars liquor is sent to dehydration process.

2.2.2 Dehydration reaction

Dehydration reaction is carried out following these conditions: atmospheric pressure and at boiling temperature of the aqueous solution with xylose, sulfuric acid as catalyst and the additional inorganic salt (NaCl) as promoter. The catalyst and xylose concentration is according to the conditions of the dilute-acid hydrolysis stage (i.e., condition 1: H_2SO_4 to 2% v/v and condition 2: H_2SO_4 to 10% v/v). The amount of NaCl added to the solution as promoter is 2.4g [10]. The experiment is performed by stirring the aqueous solution at 500rpm for 1.5 h.

2.2.3 Aldol-condensation reaction

Aldol-condensation reaction is carried out in a batch and completely sealed reactor employing $MgO\text{-}ZrO_2$ as catalyst [12]. A 5.5ml reactant solution (55 wt. % total organics, furfural/acetone= 1 by moles, methanol/water= 1.85 by volume) and 40 mg catalyst are added to the stainless steel reactor with a total capacity of 11 ml. Subsequently, the reactor is heated up to 120ºC and pressurized at 7-10 atm for 24h. Samples are taken at the initial (t = 0 h) and the end (t =24 h) part of the procedure. The temperature and pressure are controlled by an oven (Thermo Precision model 6545) and vapor fraction of the reactant solution, respectively.

2.3 Sample analysis

2.3.1 Sugars and furan-based compounds determination

Sugars and furan-based compounds during the acid hydrolysis, dehydration and aldol-condensation reactions are quantified by the HPLC system (ELITE LaChrom) using an ORH-801 Transgenomic® column. Sulfuric acid (0.01N) is used as mobile phase. The column oven and RID are maintained at 50ºC, and flow rate for mobile phase is fixed at 0.8 ml min-1 [17]. The samples are centrifuged, diluted and filtered using membrane GV (Durapore) 0.22µm of pore and 13mm of diameter into the HPLC vials. Peaks are detected by the RI detector and quantified on the basis of area and retention time of the standards (glucose, xylose, furfural and HMF) procured from Merck, Sigma–Aldrich and Acros Organics.

2.3.2 Alkane precursor determination

Alkane precursor (4-(2-furyl)-3-buten-2-one) identification is based on mass spectra (EI, 70 eV) from a gas chromatograph (Agilent Technologies 6850 Series II) equipped with a mass selective detector (MSD 5975B). The injector temperature is kept at 250 °C. The chromatographic separation is performed using a HP-5MS capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). Helium (99.99%) is used as the carrier gas with a constant flow rate of 1 mL min^{-1} and a 1:100 split ratio. The GC oven temperature is programmed from 40 °C (2 min) to 250 °C with the heating rate of 5 °C min^{-1}, and hold up during 2 min. Mass spectra and reconstructed chromatograms are obtained by automatic scanning in the mass range m/z 40–350 at 3.5 scan s^{-1}. Chromatographic peaks are checked for homogeneity with the aid of the mass chromatograms for the characteristic fragment ions [18].

2.4 Simulation procedure and techno-economic analysis

For a given raw material, flowsheet synthesis is carried out using process simulation tools. The obtained yields in experimental procedure and the operating conditions before mentioned are used as starting point for the simulation in order to select the raw material with the lowest production cost and less emissions. The process for jet fuel precursor production considered as base line 1 ton h^{-1} of raw material. The objective of the simulation procedure is to generate the mass and energy balances from which the raw materials, utilities, and energy requirements are calculated. The main simulation tool used is the commercial package Aspen Plus v8.2 (Aspen Technology, Inc., USA). Non-Random Two-Liquid (NRTL) thermodynamic model is applied to calculate the activity coefficients of the liquid phase and the Hayden-O'Conell equation of state is used for description of the vapor phase.

The capital and operating costs are calculated using the Aspen Process Economic Analyzer software (Aspen Technologies, Inc., USA). This analysis is estimated in US dollars for a 10-year period at an annual interest rate of 17% (typical for the Colombian economy), considering the straight line depreciation method and a 25% income tax. Prices and economic data used in this analysis correspond to Colombian conditions such as the raw material costs, income tax, labor salaries, among others. This data is used to evaluate the production costs per kilogram of product. **Table 2** summarizes the economic data used in the process scheme.

Table 2 Price/cost of feedstock, utilities and products used in the economic assessment.

Item	**Unit**	**Price**
SCB [a]	USD/ton	15
CCS [a]	USD/ton	18
FB [b]	USD/ton	5.7
Sulfuric acid [c]	USD/kg	0.094
Acetone [c]	USD/kg	0.97
Methanol [d]	USD/kg	0.35
2-furyl 3-buten-2-one (FA) [d]	USD/kg	5.0
Water [e]	USD/m^3	0.74
Electricity [e]	USD/kWh	0.14
Medium pressure steam [f]	USD/ton	8.18
Low pressure steam [f]	USD/ton	1.57
Fuel [g]	USD/Megawatt	24.58
Operator labor [e]	USD/h	2.56
Supervisor labor [e]	USD/h	5.12

[a] Taken from [19].
[b] Estimate: based on transport cost.
[c] Taken from ICIS pricing [20].
[d] Taken from Alibaba International Prices [21].
[e] Typical prices in Colombia.
[f] Taken from [19].
[g] Estimated cost of gas to a period range of 2015 – 2035 [22].

2.5 Environmental analysis

The environmental analysis is carried out using the Waste Reduction Algorithm (WAR Algorithm) designed by the Environmental Protection Agency of the United States (USEPA) through WARGUI software. This algorithm is based on the determination of the Potential Environmental Impact (PEI), which is a conceptual quantity representing the average unrealized effect or impact that mass and energy emissions would have on the environment [23]. The PEI are quantified in Human Toxicity Potential by Ingestion (HTPI), Human Toxicity Potential by Exposure (HTPE), Aquatic Toxicity Potential (ATP), Terrestrial Toxicity Potential (TTP), Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Photo-chemical Oxidation Potential (PCOP) and Acidification Potential (AP). Some PEI's of compounds such as lignin, cellulose and hemicellulose are not in the database of WARGUI software, so they are taken from several material safety data sheet, articles, among others.

3. Results and discussion

3.1 Acid hydrolysis

There are different parameters that determine the products formation, in this sense, the reaction time and acid concentration in the acid hydrolysis play an important role. For this reason, two operation conditions are evaluated. According to the results in **Table 3**, the reaction time of SCB has a positive effect in the production of xylose and the acid concentration helps to increase the concentration of furfural as by-product. In the CCS and FB cases, these parameters have different effects. The sugar and furfural concentration has not a significant change in the two evaluated hydrolysis conditions. Generally, the furfural is considered as an inhibitor compound when a further fermentation process is carried out. On the other hand, furfural is an interesting product and a platform to obtain the precursor of jet fuels.

The high content of hemicellulose in SCB allows to obtain high yields to xylose. On the contrary, CCS has a relative high content of hemicellulose but the xylose yield is not as high as expected. This situation can be attributed to the timber structure of the material that prevents the correct action of the acid. Despite the low content of hemicellulose in the FB, the yield can be considered interesting due to the few information that is reported of the behavior of this material when is subjected to these type of processes.

Table 3 Results of the acid hydrolysis.

Raw material	Condition 1		Condition 2	
	g xylose/g hem	g furfural/g hem	g xylose/g hem	g furfural/g hem
SCB	0.81±0.004	0.054±0.001	0.60±0.016	0.076±0.003
CCS	0.50±0.030	0.024±0.002	0.51±0.010	0.023±0.002
FB	0.58±0.017	0.019±0.003	0.54±0.025	0.017±0.001

hem: hemicellulose

3.2 Dehydration

Furfural is considered a highly versatile and key chemical platform in the manufacture industry of a wide range of important chemicals. The future demand of furfural seems to increase in different fields, such as plastics, pharmaceutical, energy and agrochemical industries [24], [25]. Rong et al. (2012) reported that the production of furfural from lignocellulosic biomass has a yield of 75% using as catalyst 10 %w/w of sulfuric acid. Additionally indicates that xylose dehydration to furfural has a yield below 10% when acid concentration is nearly to 2.5% w/w. On the other hand, , the yield reduces to 51% when the concentration of sulfuric acid reaches 12.5% w/w[10].

In this work, the acid concentrations are 2 and 10% v/v for the operation conditions 1 and 2, respectively. **Table 4** present the furfural yields for the two evaluated conditions. Raw materials evaluated in the conditions 1 and 2 have an average yield of 0.071 and 0.057 grams of furfural per gram of xylose, respectively. These results show a significant trend with the data reported due to when there is low concentrations of acid the yields coincide to be near to 10%. The report indicates that if there is high concentrations of acid, the yields tend to be low. The same situation occurs in the evaluation made in this work. In general, low yields of furfural can be attributed to side reactions, such as dehydration of xylose into other aldehydes (e.g., formaldehyde) and degradation of furfural or polymerizations of intermediate, and furfural [10].

Table 4 Results of dehydration reaction.

Raw material	Condition 1 (g furfural/g xylose)	Condition 2 (g furfural/g xylose)
SCB	0.060±0.008	0.060±0.005
CCS	0.063±0.002	0.067±0.005
FB	0.092±0.009	0.045±0.005

3.3 Aldol-condensation reaction

Table 5 shows the percentage of disappearance of furfural as the main reagent in the aldol-condensation reaction for operation condition 1 of each raw material. **Figure 3** presents the chromatograms that indicate the qualitative appearance of precursor (4-(2-furyl)-3-buten-2-one). The obtained spectrums are compared with the spectra of the NIST database that counts with the chromatography equipment with a probability of 96%. The catalytic performance is evaluated based on the two factors mentioned before. According to the results, specifically the percentage of disappearance of furfural, the MgO-ZrO_2 as catalyst exhibits excellent catalytic activity with a maximum furfural conversion of 96.5% for CCS and minimum of 71.7% for SCB after reaction for 24h at 120ºC in a batch reactor.

The data reported in literature indicate a disappearance percentage of 66% in the same conditions of the procedure developed in this work [12]. The results from this work show clearly the potential of lignocellulosic biomass to obtain liquid alkanes range jet fuels. Besides, these results indicate the promising future of furan-compounds as platform products to obtain biofuels and great amount of chemicals.

When aldol-condensation reaction is carried out for operation condition 2, the formation of interest products is not recorded for any raw material. The aldol-condensation reaction is assessed with the following conditions: i) excess of catalyst, ii) excess of acetone, iii) normal load of catalyst and iv) lower than normal catalyst loading, but in none of the cases there is presence of the precursor. This behavior can be explain due to the high concentration of the homogeneous catalyst (H_2SO_4) in acid hydrolysis and dehydration steps which can inhibit the heterogeneous catalyst (MgO-ZrO_2). Moreover, unwanted reactions can encourage forming magnesium sulfates and/or zirconium. A solution to this problem can be the implementation of a detoxification process prior to the aldol-condensation reaction in order to reduce the high content of sulfuric acid and promote the correct action of the heterogeneous catalyst.

Table 5 Results of aldol-condensation reaction.

Raw material	Condition 1 (% disappearance of furfural)	Condition 2 (% disappearance of furfural)
SCB	71.7±0.018	*Nd*
CCS	96.5±0.014	*Nd*

FB	92.9±0.008	*Nd*

nd: non-determined

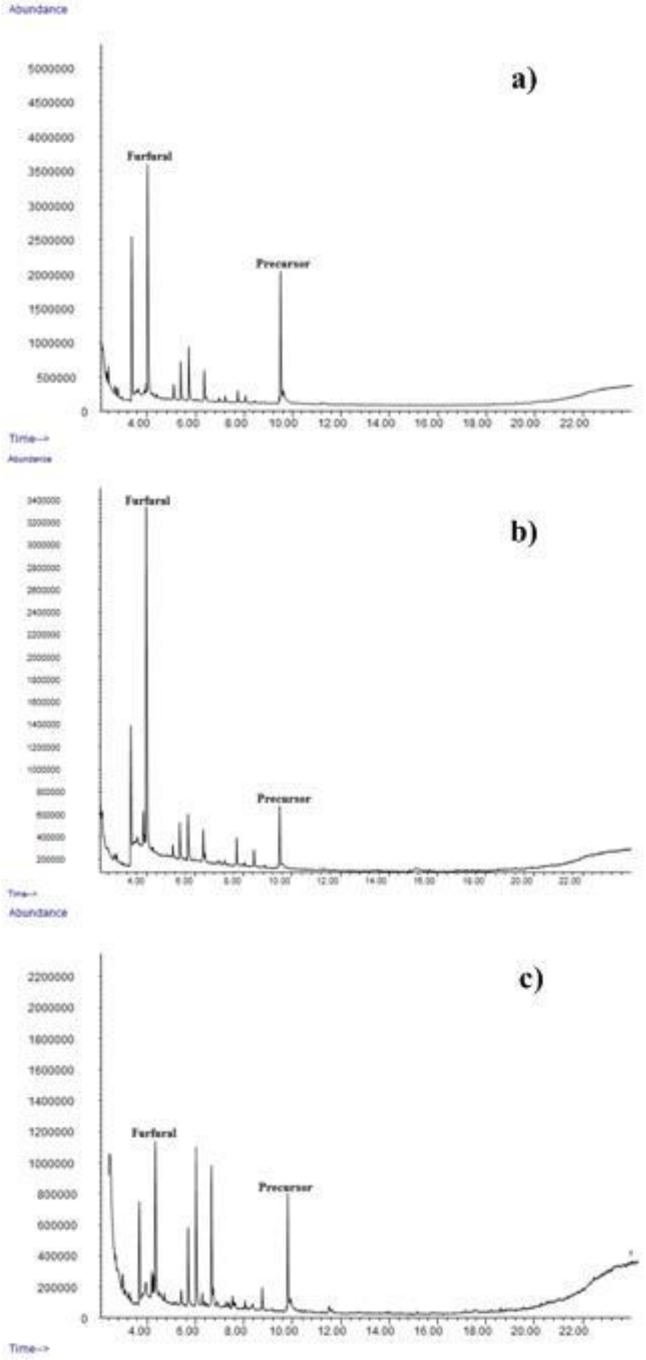

Figure 3 GC-MS chromatographs of furfural and precursor when a) SCB, b) CCS and c) FB are used as raw material.

3.4 Simulation results

The simulation procedure only is carried out for the experimental yields of the operation conditions 1. In the case of operation conditions 2, the process simulation is not able due to the reasons mentioned above. According to results from the technical assessment, SCB, CCS and FB have relative high FA yields 0.14, 0.13 and 0.08 grams of FA per gram of lignocellulosic biomass, respectively. The good content of hemicellulose in these residues, the efficiency in acid hydrolysis and dehydration stages, involve good flows of product.

Figure 4 summarizes the economic and environmental results for SCB, CCS and FB to produce jet fuel precursor. The total costs distribution for each raw material is directly related with four parameters such as depreciation, operating cost, utilities cost and reagents cost. The utilities cost represents approximately more than 50% of total production cost which is related with the great amount of energy that demands the aldol-condensation reaction to generate the FA. As can be seen there are not significant changes in the percentages of distribution between the residues. When CCS is used as source of FA, the utilities cost is slightly reduced a 5% with respect to others materials and this value is assumed in the reagents cost. When SCB is used as raw material, the reagent costs are slightly higher than for other raw materials. The mild reduction in utilities cost is associated with the demand of low pressure steam. For SCB, CCS and FB a total capital cost of 6.6, 5.9 and 6.4 USD millions is obtained, respectively.

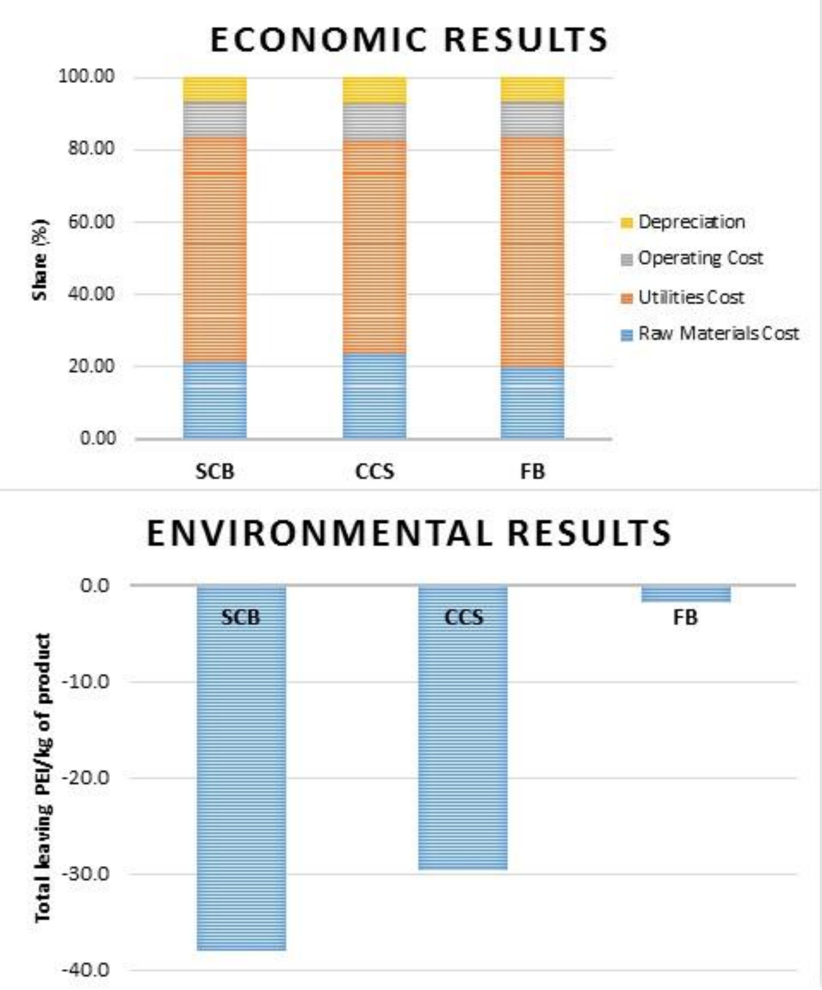

Figure 4 Economic and environmental results for SCB, CCS and FB to produce jet fuel precursor.

According to the obtained results, the production cost is 6.02, 5.57 and 10.22 USD per kilogram of precursor for SCB, CCS and FB, respectively. In this sense, the economic margins are -20.45, -11.41 and -104.34% for SCB, CCS and FB, respectively. The reduction in the utilities requirements, the composition and cost of raw material, and the yields are important factors that contribute to obtain a moderate negative economic margin in the case of SCB and CCS. These values can conducted to better answers if other elements are considered such as the commercial use of the released energy, the optimization of operation conditions and the integration of process under a biorefinery concept to generate other products that subsidize the operating costs.

The environmental assessment is based on the criteria of the potential environmental impacts, described in section 2.5. The results show that the best process, from the environmental point of view, is the one that considers the production of FA from SCB followed by CCS and FB, as indicates in **Figure 4**. In the total PEI per kilogram of product, impacts as human toxicity by ingestion (HTPI) and terrestrial toxicity (TTP) affect the most to the total environmental impact. The HTPI and TTP potentials are high due to the organic waste in the liquid streams leaving the process. However, the released energy in the process compensates the polluting waste effluents. SCB is the process with greater flow of FA and released energy that can be exploited, consequently is the friendliest environmental process.

4. Conclusions

This work contributes to the implementation of simultaneous processes for the transformation of agroindustrial wastes to obtain sugars, furan-based compounds and precursor of liquid alkane range jet biofuel, focusing on the comprehensive utilization of raw materials. Additionally, this work shows that MgO-ZrO_2 catalyst allows converting carbohydrate-derived compounds, like furfural, to water-soluble intermediates (precursor FA). These compounds are the base for future production of liquid alkanes.

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