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Agrorefinery Synthesis Using Empty Palm Fruit Bunches as Feedstock via Superstructure Optimization

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In this work has synthesized two superstructures that encompass technological alternatives applicable to the empty fruit discarded bunches on extract palm oil process to produce ethanol, bio-fertilizer and substrate for animal feed under agrorefinery concept. A bibliographic review of processes was realized where technologies or conversion operators, chemical species generated and the actual yields of each of them were checked. Superstructures were limited to a maximum of five layers of conversion operators, considering chemical and physical transformation technologies. The best topology of agrorefinery was selected using process optimization based on the production yield of the final products. As results, it was observed that branches of the superstructure that present the best yields for ethanol production had the simultaneous saccharification and fermentation (SSF) technology. This technology is better than the separated hydrolysis and fermentation (SHF) technology but requires operating conditions that are suitable for both the hydrolytic enzymes and the microorganisms involved in the processes steps. About biofertilizers and, substrate for animal feed, the technology of mycotic treatment with *Pleurotus sajor-caju* then a sludge co-composting and phytoremediation of effluent presented satisfactory results.

1. Introduction

Currently, oil is the principal source of energy that covers many human needs, but its production and subsequent use generate negative effects on the environment. Therefore, the production of bioenergy and biomaterials has a high potential to satisfy the growing demand and valorising waste, taking advantage of them as a renewable raw material. (Perez et al., 2016). During the palm oil extraction process, different wastes are obtained which can be used in diverse ways. Among these are: (i) the empty tusks (rachis) which fertilizers, boiler fuels and raw material for paper production can be obtained; (ii) muddy waters containing chemical substances from the nutrients and fertilizers that are supplied to the palms; and (iii) the dish that has a high calorific value and can be used as a domestic fuel, in stoves and in boilers (Garcés and Cuellar, 1997). In this sense, it is necessary a progressive change in the use of fossil fuels to the use of biological-based supplies. In this way, there is an excellent perspective on the progress in integrating and multifunctional biorefineries. The objective of this research is to synthesize Agrorefinery topologies for the use of the discarded rachis during the process of extracting oil from the African palm to obtain ethanol, biofertilizer, and substrate for animal feed (Budzinski and Nitzsche, 2016).

2. Metodology

For the creation of the superstructures, bibliography review was done to know the characteristics of the waste to work and the technologies that can be applied to obtain ethanol and other products from these. This information was collected in two superstructures: one to produce ethanol from the rachis, and the other superstructure to produce biofertilizer, and substrate for animal feed from distillers vinasse. The list of conversion operators was organized, involving the appropriate technologies for the use of the rachis and vinasse and their respective chemical species; finally, the conversion operators and chemical species were linked getting as result the superstructures. The agro-refinery proposal is based on information provided by a palm oil extractor located in the municipality of María La Baja, Bolívar- Colombia, where the flow of entrance to the process is equivalent to 30,000 kg / h of fresh palm oil fruit clusters with a production of empty fruit bunches (EFB) or rachis of 12765.75 kg / h, this will be the mainstream of the process.

3. Results and Discussion

3.1 Synthesizing superstructures under the concept of Agrorefinery for the use of palm rachis in the production of ethanol, biofertilizer, and substrate for animal feed

The rachis is composed mainly of hemicellulose ($C_5H_8O_4$), cellulose ($C_6H_{10}O_5$), and lignin. Figure 1 shows the superstructure that synthesizes the processes and the technologies applicable to lignocellulosic materials for obtaining ethanol. First, a pre-treatment is carried out to eliminate barriers that prevent the transformation of the biomass (Piñeros, 2014). Then, thermochemical processes such as pyrolysis and gasification can be applied, if one of these technologies is used and subsequent synthesis of CO and H_2 it is possible to obtain ethanol (Urien, 2013) (García, 1993). Ethanol can also be obtained by applying integration strategies of processes such as separate hydrolysis and fermentation SHF, simultaneous saccharification and fermentation SSF, simultaneous saccharification and co-fermentation SSCF and finally the consolidated bioprocess (Quintero, 2009). The mixture of ethanol resulting from the fermentation can be subjected to fractional distillation and achieve a concentration of 96%. Due to this mixture is Azeotropic, it is necessary to apply some technologies such as Azeotropic distillation, extractive, vacuum distillation, sieves molecular or pervaporation, able to purify ethanol at high concentrations like 99.5% which is the established value for use in internal combustion engines in the country.
On the other hand, because of the distillation of ethanol vinasses of high organic material are obtained that must be treated for reducing their power of contamination. Figure 2 shows a superstructure that collects technologies to manage this waste and get a valued product such as biofertilizer and substrate for animal feed. These can be treated with biological processes including anaerobic digestion, aerobic fermentation or treatment with microalgae (Phytoremediation). The biomass obtained after the application of anaerobic or aerobic treatments can be sedimented, centrifuged or filtered to obtain a substrate for animal feed. To improve the susceptibility of vinasse to biological treatments, a pre-treatment with ozone or fungal pre-treatment can be applied, the fungal pre-treatment with lignolithic fungi can biodegrade toxic and recalcitrant compounds (Castro and Parra, 2011). Another option is the concentration of the vinasse by vaporization and subsequent incineration to use the ashes as biofertilizer due to its high content of potassium. Also, vinasse concentrated by evaporation can be dried to produce a solid containing all the salts and original organic material or used to produce biofertilizer by Co-composting (Alonso, 2016).

3.2 Select the most appropriate Agrorefinery topologies from the point of view of theoretical yield

According to the synthesis superstructure for obtaining ethanol, the selected pre-treatment technology (Table 1) was Liquid Hot Water (LHW) with a percentage of lignin removal of 69% and hemicellulose hydrolysis of 80%. Depending on the stages of hydrolysis and fermentation of the lignocellulosic matrix and according to the percentages of yields compiled in tables 2 and 3, the technology that allows a greater obtaining of ethanol is Bioprocess Consolidated, however, for this study, the selected technology was simultaneous saccharification and fermentation due to the maturity of its information.

Table 1: Compilation of yields of the pretreatments synthesized in Figure 1

Pretreatment technology	Lignin Removal (%)	Hemicellulose Hydrolysis (%)	References
Alkaline hydrolysis (AP)	55-60	50	Dahnum et al, 2015, Waheed et al, 2017
Organosolv (OP)	63	80	Quintero, 2009, Prasad et al, 2013
Diluted Acid Hydrolysis (AD)	18	80 (With H_2SO_4)	Sánchez et al, 2010, Waheed et al, 2017
Steam Explosion (SEPD)	40–45	80	Sánchez et al, 2010, Waheed et al, 2017
Liquid Hot Water (LHW)	69	80	Sánchez et al, 2010, Waheed et al, 2017

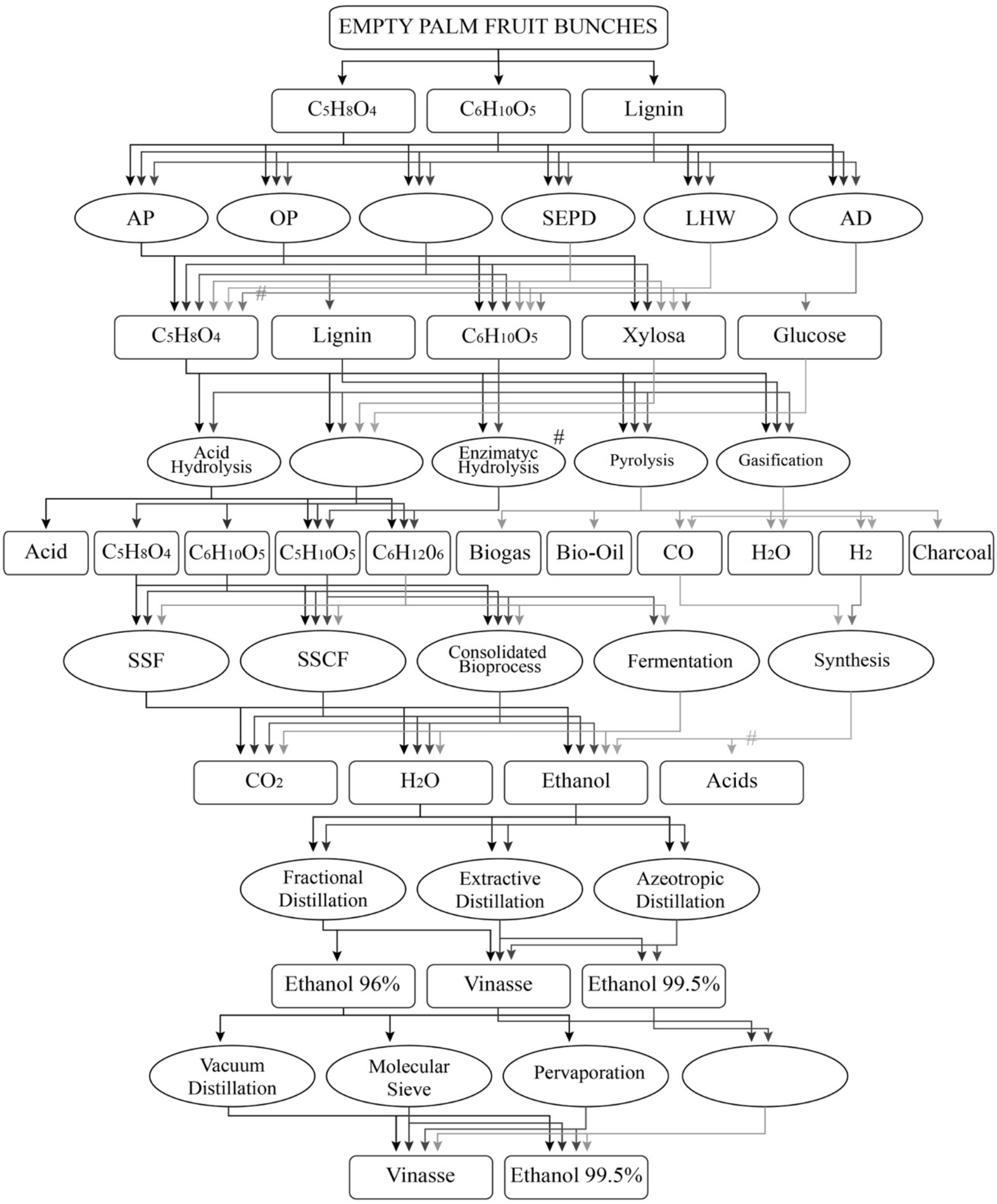

Figure 1: Superstructure to produce ethanol from rachis.

Table 2: Compilation of reactions and real performances of the technological routes synthesized in figure 1

	Technological routes	Products	Yield (%)	References
Cellulose	Pyrolysis	CO	18,6	Bao et al, 2012
		H_2	4	Antal y Gronli, 2003
		Biocarbon	12	Urien, 2013
Cellulose	Enzymatic hydrolysis	$C_6H_{12}O_6$	70,2	Bao et al, 2012 Molina, 2012
Hemicellulose	Enzymatic hydrolysis	Sugar	83	Bao et al, 2012
Cellulose	Gasification	CO	50	Bao et al, 2012
		H_2	7	
CO	Synthesis	Alcohol	20,8	Bao et al, 2012

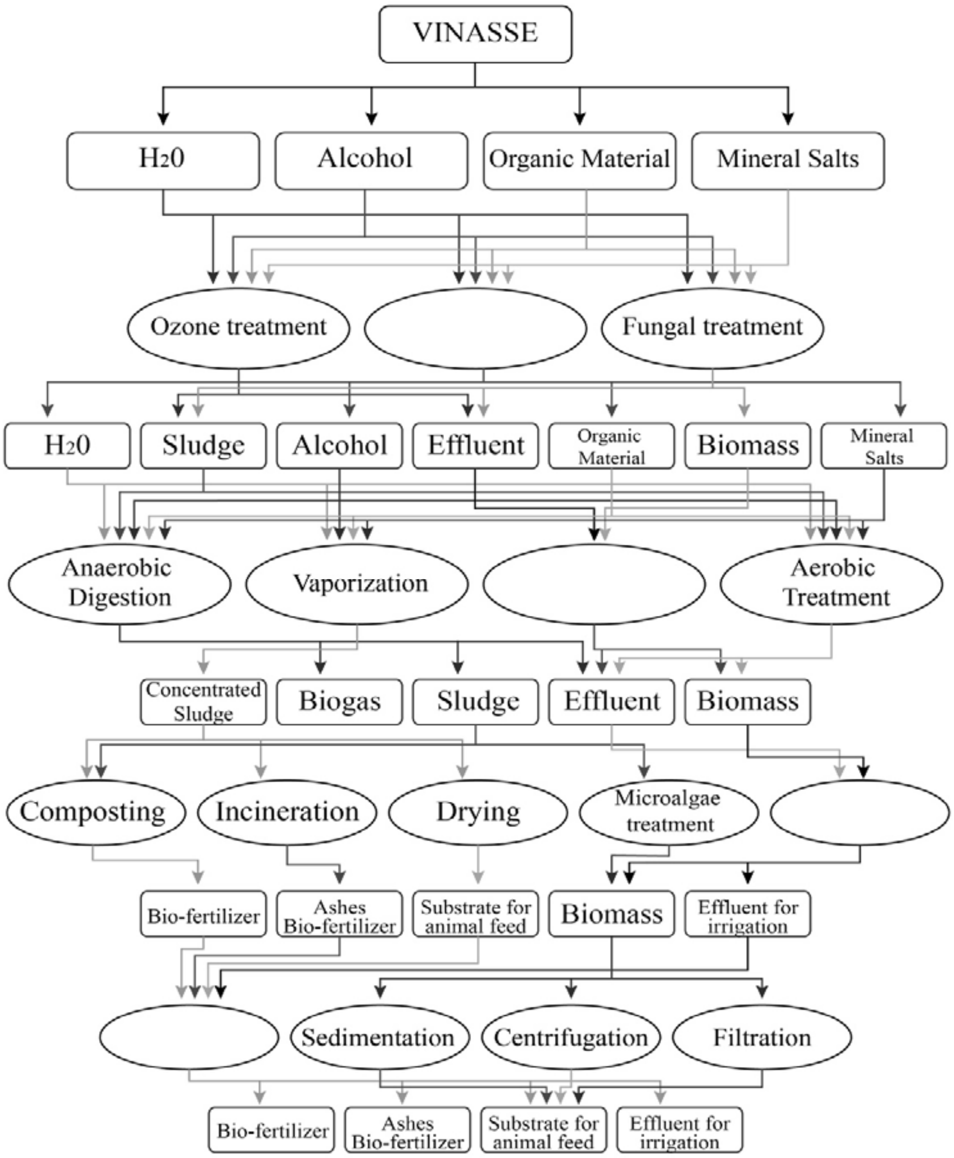

Figure 2: Superstructure for obtaining biofertilizer and substrate for animal feed from Vinasse

Table 3: Compilation of real yields of the integration strategies of Hydrolysis/Fermentation processes

Hydrolysis and fermentation	Conversion of Cellulose to Glucose	Conversion of Glucose to Ethanol	Conversion of Xylose to Ethanol	References
SHF Diluted acid hydrolysis	87%	76%	70-80%	Dahnum et al., 2015 Quintero, 2009
SSF	88%	92-96%	80-95%	Quintero, 2009
SSCF	80%	92%	95%	Quintero, 2009
CDP	90%	92-95%	92-95%	Quintero, 2009

To obtain a 99.5% ethanol and, according to (Sanchez, 2008), the purification technology that allows a higher concentration is the azeotropic distillation. However, the technology selected was extractive distillation because it is produced more ethanol in the resulting mass flow through this purification technology. According to the results presented by Cuello and Mendoza (2017) in table 4 for the superstructure of the vinasse and regarding of Chemical Demand Oxygen COD removal, the best pre-treatment is with the fungal *Pleurotus sajor-caju*. After this, aerobic biological treatment is applied according to the percentages of COD removal.

Table 4: Compilation of the removal yields of the biological and physicochemical treatments

Treatments		Removal COD (%)	Removal BOD (%)	Color removal (%)	Removal phenols (%)
Treatment with ozone		27	-	80	-
Fungal treatment	*Pleurotus sajor-caju CCB020*	82,8	75,3	99,2	-
	P. chrysosporium	47,48 a 25°C 54,21 a 39°C	-	45,10 a 25°C 56,81 a 39°C	54,72 a 25°C 59,41 a 39°C
	Trametes sp.	61,7	-	73,3	-
	Penicillium sp	52,1	-	-	70
	Penicillum decumbens	50,5	-	-	70
Anaerobic digestion (Without pretreatment)		70	-	-	-
Anaerobic digestion (With pretreatment with ozone)		80	-	-	-
Aerobic treatment (Without pretreatment)		84	-	-	-
Treatment aerobic (With pretreatment with ozone)		53-87	-	-	48-83
Phytoremediation	*Chlorella vulgaris*	30,92	30,92	-	-
	Spirulina platensis	40-50	-	-	-

With the objective of obtaining enough biomass destined to the production of a substrate for animal feed, the effluent generated in the aerobic treatment with *Spirulina platensis* can be brought under a microalgae treatment, it is one of the most used due to its high COD removal capacity. Also, the sludge generated can be used to produce biofertilizer by Co-composting. Table 5 shows the selected topologies distributed in conversion operators, chemical species and the mass balance for the proposal of agrorefinery.

Table 5: Topologies selected for the production of ethanol from rachis and biofertilizer and substrate for animal feed from vinasse.

Topology One			Topology Two		
Conversion Operators	Chemical Species.	Mass flow kg/h	Conversion Operators	Chemical Species	Mass flow kg/h
EFB 12766 kg/h	Water	8400	Vinasse 45515.72 kg/h	Water	39821.07
	Other substance	7972		Alcohol	4.5
	Lignin	1454		Organic material	5131.54
	Cellulose	2140		Mineral Salts	558.61
	Hemicellulose	1198		Pleurotus sajor-caju	798.58
LWH	Lignin in H_2O	12786	Mycotic Treatment	Residual Water	40800.94
	Other substance	4950		Biomass	5513.36
	Xylose	945			
	Cellulose	2278			
	Hemicellulose	208			
	Water	42063			
SSF	Ethanol liquor	49016	Aerobic Treatment	Rachis (Added)	73.96
	CO_2	1427		Mud	174.27
				Effluent	39805.9
Fractional distillation	Ethanol	3500		Chlorella Vulgaris	5970.89
	Vinasses	45516		Biomass	822.77
				Effluent for irrigation	27498.81
Extractive distillation	Ethanol	1084	Centrifugation	Biofertilizer	246.23
	Water	2416		Substrate for animal feed	4170.62
				Effluent for irrigation	41606.16

With the selected topologies, the scheme of an agrorefinery was proposed for the use of the residual rachis of the African palm oil production process, obtaining as products: ethanol for use as biofuel, biofertilizers, a substrate for animal feed and effluent for irrigation use. Regarding the production of ethanol from the agrorefinery, a yield of 0.09 kg of ethanol was obtained per kg raw material feed. This result is higher than that obtained by Pereira et al., (2015) in its proposed process of joint production of bioethanol from sugar cane with 0.045 kg of ethanol per kg of raw material fed. These results allow demonstrating the potential of the use of the proposed agrorefinery. Regarding the use of the vinasses, no similar studies were found to obtain fertilizer, effluent for irrigation and substrate for animal feed in a simultaneous manner, what allows the comparison of the obtained results. This part of the agrorefinery is a proposal got to use the percentage of COD removal in industrial wastewater. It is expected to be the basis for future research.

4. Conclusions

The topology that exhibits the best results from of the point of view of the yield of production of ethanol is the formed for a pre-treatment with Liquid Hot Water (LHW) followed by Simultaneous Saccharification and Fermentation (SSF) and a subsequent fractional and extractive distillation producing 1084 kg/h of ethanol, which corresponds to 1373 L/h. About the use for vinasses residual of the ethanol production process, the most promising route involves a mycotic treatment with *Pleutorus sajor-caju*, an aerobic treatment followed by a co-composting of sludge and microalgae treatment of effluents, obtaining 246 kg/h of biofertilizer, 4171 kg/h of substrate for animal feed and 41606 kg/h of effluent for irrigation from 45515.72 kg/h of vinasse. This agro-refinery would allow the chain of African Palm in Colombia to be valued and to diversify the products that currently are only focused on oil production.

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