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Development of a Hybrid Methodology for Synthesis of Biofuels Production Processes Based On Optimization of Superstructures

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Biofuels can be obtained using different processing routes and raw materials, so there are infinite combinations of possible topologies for raw material processing; it is desirable to develop a methodology for evaluation of different combinations in order to select the pathway that best accomplish a specific criterion. In this paper, the authors developed a hybrid methodology for the synthesis of biofuel production processes, based on a branch of available products and intermediates, the establishment of a superstructure with technologies and chemical species involved, mathematical optimization of production routes and depth assessment of the most promising alternatives.

As a case of study, the methodology is applied in the synthesis of a process of production of biofuels from wastewater. The results showed correspondence between intermediate and final products for biodiesel and hydrogen, and the superstructure was constructed based biodiesel as main product. The optimization of the superstructure showed that the most promising route is through hydrothermal liquefaction of organic slurry and hydroprocessing of biocrude, with a maximum product yield of 0.61 tonnes of biodiesel/tonne of biomass.

1. Introduction

There is a growing interest in the identification of cost-effective, clean, and renewable sources of energy. Biofuels are among the most promising alternatives as they offer many benefits related to energy security, economic stability and reduction of the environmental impact of greenhouse gases (Brunet, et al., 2014). Third-generation biofuels are produced from non-conventional feedstocks as microorganisms (yeast, fungi and microalgae), being the most common biogas, biodiesel from lipids, and bioethanol from reducing sugars (Barajas-Solano et al., 2014). Microorganisms can grow in domestic and industrial wastewaters, where they uses the organic matter present in these effluents as feed, so it is common to find biomass in pools of wastewater treatment plants. Composition of biomass can determine the feasibility of a biofuel or high value substances production process (Pinzon Frias et al., 2014). By using wastewater as a culture medium for the growth of third generation energy feedstocks can be produced a double benefit, reduction of organic load of the effluent and generation of usable biomass for biofuels and high added value products (Mata et al., 2014).

On the other hand, the conceptual design of processes belongs to the area of chemical process synthesis, which was pioneered by authors as Douglas (1988) and Rudd & Watson (1968), process synthesis has had an important impact in the development, of chemical processes, providing systematic methodologies for identifying flowrates, design conditions and optimal networks. Several advances in process synthesis has been achieved in recent decades, taking into account proposed strategies, tools and frameworks for process synthesis, three types of approaches can be differenced: heuristic-based approaches which uses specialized knowledge of a process and specific experience, mathematical programming-based approaches which uses a

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superstructure optimization formulation with an objective function desired, and hybrid approaches, which combines both hierarchical decomposition and mathematical programming (Yuan et al., 2013).

Taking into account the enormous number of possible combinations of processing routes, it is necessary the development of a methodology for selecting the most convenient pathway for biomass transformation under a specific parameter, in this paper is shown the development of a process synthesis methodology that integrates various concepts as direct and inverse branching and superstructure optimization, and its application taking as a feedstock a biomass from a wastewater treatment plant with a known composition.

2. Formulation of models for superstructure optimization

The superstructure contains a number (NP) of layers of chemical species designated under the index *i* , and (NP - 1) layers of processing technologies, designated by the index *k*. Performance model for the extraction of metabolites and processing in the k^{th} layer flows in the related chemical species into and out of the conversion operator, namely:

$$(F^{out}_{g_i,k,1},...,F^{out}_{g_i,k,c},...,F^{out}_{g_i,k.NC}) = \psi_{g_i,i}\ (F^{in}_{g_i,k,1},...,F^{in}_{g_i,k,c},...,F^{in}_{g_i,k.NC},d_{g_i},O_{g_i}) \quad \forall g_i\ ,\ \forall k \tag{1}$$

Where $F^{out}_{g_i,k,c}$ and $F^{in}_{g_i,k,c}$ are the flowrates in tonnes per year of chemical species c leaving and entering transformation technology g_i in layer *k*. The design and operating variables of each technology g_i are denoted by d_{g_i} and O_{g_i} , respectively. The mass balance of chemical species *c* of the chemical species *i* in the technology layer extraction / transformation layer *k* is given as follows:

$$F_{c,k+1} = F_{c,k} + \sum_{g_i} r_{g_i,c,k} \quad \forall g_i\ ,\ \forall k \tag{2}$$

For including the economic criteria into the optimization, the term total annualized cost (*TAC*) is introduced, and is defined as the summation of annualized fixed costs (*AFC*) and annual operating costs (*AOC*) (e.g., El-Halwagi, 2012).

$$TAC = AFC + AOC \tag{3}$$

The annualized fixed costs $\left(AFC_{g_i,k}\right)$ of technology evaluated g_i in layer *k* is given by a cost factor ($\alpha_{g_i,k}$) times the flowrate of the limiting component entering the transformation technology, or the flowrate of the feedstock containing the chemical specie to extract, capacity differences between data reported in literature and this work were adjusted using the seven tenths factor rule, because it applies for large equipment and because it is a new and untested process so it's necessary to be more conserved in the use of technologies to scale, additionally it is a number that has proven successful in the optimization of superstructures (Bao et.al 2011).

$$AFC_{g_i,k} = \alpha_{g_i,k}(F^{in}_{g_i,c^{\lim}_{g_i},k})^{0.7} \tag{4}$$

The annual operating costs $\left(AOC_{g_i,k}\right)$ of technology evaluated g_i in layer *k* is given by a cost factor ($\beta_{g_i,k}$) times the flowrate of the limiting component entering the transformation technology, or the flowrate of the feedstock containing the chemical specie to extract, i.e.

$$AOC_{g_i,k} = \beta_{g_i,k} F^{in}_{g_i,c^{\lim}_{g_i},k} \tag{5}$$

The objective function involves the maximization of revenue derived by the selling of final product defined as the value of the product less the cost of feedstock and the *TAC* of the chemical species processing.

$$\text{Maximize } C^{\text{Product}} F_{p,NP} - \sum_{k} \sum_{g_i} TAC_{g_i} - C^{\text{Biomass}} F^{\text{Biomass}} \tag{6}$$

After the superstructure optimization, additional issues must be considered for selecting the processing topology. One of these issues is the cost of co-products obtained using the promising pathway without any further processing. Therefore, the objective function is modified as follows:

$$C^{\text{Product}} F_{p,NP} + \sum_{k} \sum_{m} C_{m,k}{}^{\text{Co-Product}} F_{m,k}{}^{\text{Co-Product}} - \sum_{k} \sum_{g_i} TAC_{g_i} - C^{\text{Biomass}} F^{\text{Biomass}} \tag{7}$$

Where C^{Product} is the selling price of the product (e.g., $/t), C^{Biomass} is the cost of the feedstock (e.g., $/t) and F^{Biomass} is flowrate of the feedstock.

3. Results

A literature review and selection of existing and emerging technologies for the production of different chemical species involved in the process was performed taking into account the information available in the literature and experimental results (Bao et al., 2011). Information of the composition of solids in wastewater, which was obtained in previous experimental unpublished work developed by authors, cost parameters for solids separation and drying if it is necessary for any technology and economic data was summarized (Table 1). In cases where no information was available on the costs of the technology applied to the biomass from wastewater, were used the economic data for the same technologies that affect similar raw materials (González-Delgado, 2014).

Table 1. Wastewater composition modelled and economic parameters for case study.

Parameter	Unit	Value
Wastewater composition (solids)		
Carbohydrates	%	10
Lipids	%	33
Proteins	%	55
Special substances	%	2
Selling price of main product	$/t	900
Processing capacity	t biomass/y	100,000
Cost of feedstock (Collecting and transport included)	$/t	50
Biomass harvesting		
Annualized fixed cost parameter for different capacity	$\$ \cdot y^{-0.3} \cdot t^{-0.7}$	97
Annualized operating cost parameter for different capacity	$/t	1.92
Biomass drying		
Annualized fixed cost parameter for different capacity	$\$ \cdot y^{-0.3} \cdot t^{-0.7}$	348
Annualized operating cost parameter for different capacity	$/t	200

Table 2 shows the results of the economic evaluation for each technology in layer k of the superstructure. Technologies such as oil or alkane secretion feature high values of α, caused by the special cultivation conditions required for obtaining the hydrocarbons related to the need to avoid the presence of undesirable microorganisms into the culture media which can consume the released products for their growth, in practical terms, these technologies based on secretion of products are difficult to be applied in wastewater treatment plants. The β values for oil and alkane secretion (which are related to the separation of desired compounds) are lower in comparison to other technologies present in superstructure. With wastewater as raw material and Biodiesel as the main product, a superstructure with chemical species obtainable from solid phase of wastewater and extraction / processing technologies (Figure 1) is built.

Table 2: Cost parameters for wastewater-to-diesel superstructure optimization from an economic point of view (Modified from González-Delgado, 2014)

Process	Product	α($\$ \cdot y^{-0.3} \cdot t^{-0.7}$)	β($/t feed)
Alkane secretion	Diesel-like	22,130.40	173.99
Direct transesterification	Diesel-like	1,001.94	439.63
Wet extraction	Lipid	869.93	194.32
Enzymatic degradation	Lipid	20,087.15	242.64
Oil secretion	Lipid	22,130.40	164.92
Solvent extraction	Lipid	929.59	309.82
Supercritical extraction	Lipid	2,383.97	479.92
Esterification/transesterification	Diesel-like	738.14	353.00
Hydrotreatment	Diesel-like	595.94	199.00
Transesterification (heterogeneous)	Diesel-like	721.77	211.87
Transesterification (homogeneous)	Diesel-like	369.07	154.55
Supercritical transesterification	Diesel-like	545.17	80.03
Supercritical Water Gasification	Methane	3,464.65	462.32
Supercritical Water Gasification	Syngas	3,464.65	462.32
Gasification	Syngas	2,976.40	423.10
Gasification	Methane	2,976.40	423.10
Pyrolysis	Bio-Oil	1,576.65	265.50
Pyrolysis	Syngas	1,576.65	265.50
HTL	Biocrude	2,869.42	227.10
Fischer-Tropsch	Diesel-like	2,409.82	150.10
Steam reforming	Syngas	2,593.16	623.40
Autothermal reforming	Syngas	1,880.04	592.23
Partial oxidation	Syngas	2,333.84	529.89
Cracking	C_2H_4	7,584.73	35.87
Hydroprocessing	Diesel-like	595.94	199.00
Oligomerization	Diesel-like	706.23	55.79

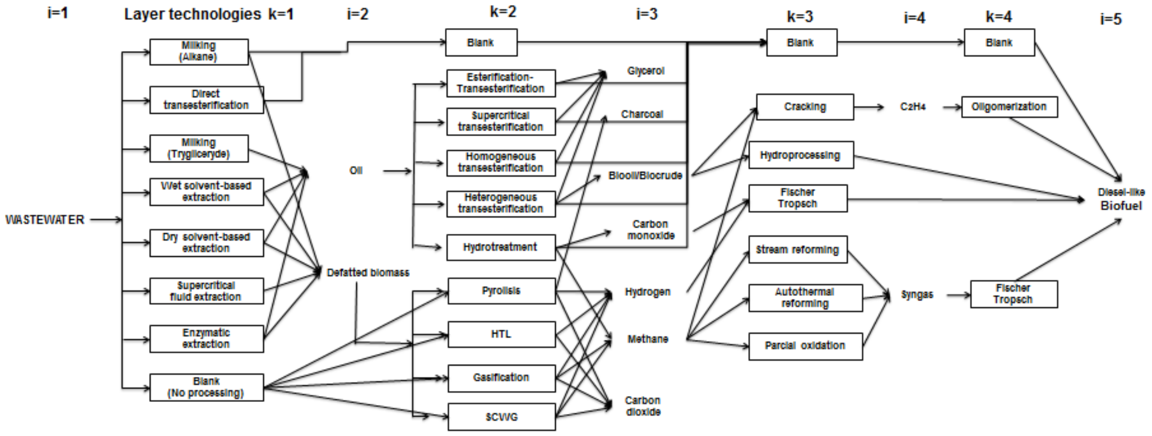

Figure 1: Superstructure of chemical species and technologies for extraction / transformation for the production of biodiesel from wastewater.

After optimization of the superstructure, only one alternative showed positive results as shown in Figure 2. The path starts with the liquefaction process of hydrothermal slurry (with biomass), which creates an aqueous phase and a phase organic, known as bio-oil or bio crude. The bio crude liquid is improved biofuel using hydroprocessing technologies, taking diesel range alkanes as the main product. The product flow on this route is 60,649 t/y of biodiesel.

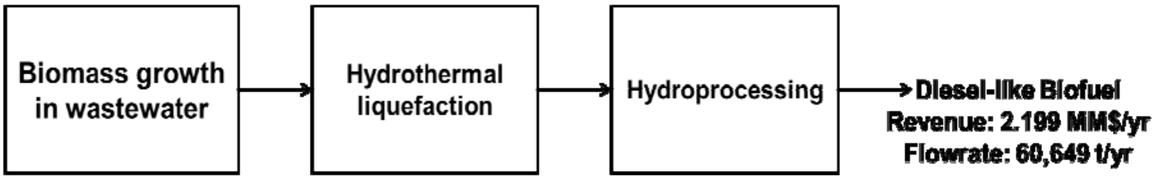

Figure 2: Optimal topology for the production of biodiesel from PTAR microbiota after optimization of the superstructure.

A schematic representation of the optimal routes superstructure obtained after application of the concept of co-product valorisation can be seen in Figure 3. For the production chain of HTL-based wastewater transformation into biodiesel, the aqueous phase obtained after liquefaction can be recycled to the first stage of the process, the main products obtained in this case of study are gasoline-like biofuel and biodiesel-like biofuel.

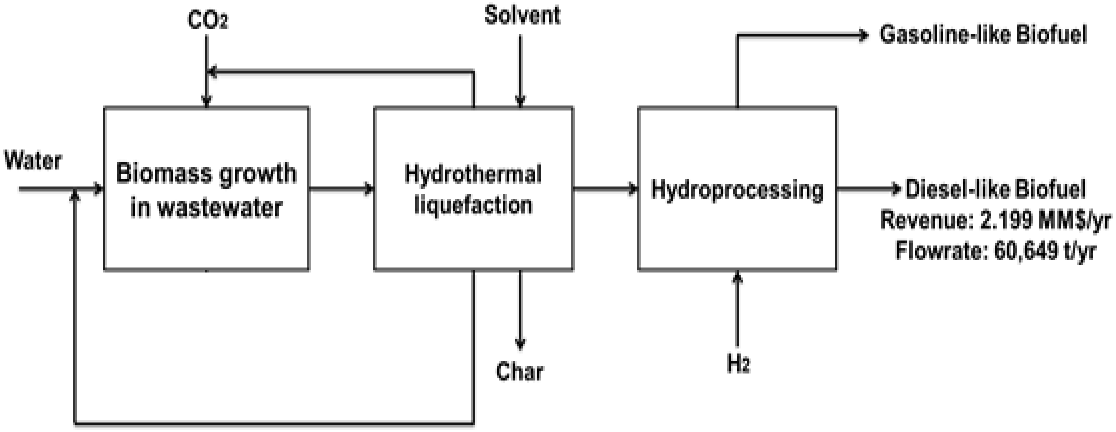

Figure 3: Solution for the superstructure maximization considering additional economic parameters taking into account the valorisation of co-products.

4. Conclusions

A methodology for the synthesis and optimization of production processes for biofuels has been proposed, the methodology is based on several integrated approaches including branching by forward and reverse selection of the main product, superstructure optimization, applying the concept of co-product valorisation, and optimized multicriteria comparison of alternatives. For the case study, the economic viability of pool- PTAR for biofuel production showed, raising the possibility of synergy with companies that handle wastewater, providing added value to the waste effluent.

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