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A. Vargas Santillán, J. C. Farias Sanchez, M. G. Pineda Pimentel and A. J. Castro Montoya*

Olefins and Ethanol from Polyolefins: Analysis of Potential Chemical Recycling of Poly(ethylene) Mexican Case

DOI 10.1515/ijcre-2015-0217

Abstract: Plastic solid waste (PSW) presents challenges and opportunities to society regardless of their sustainability awareness and technological advances. A special emphasis is paid on waste generated from polyolefin sources, which makes up a great percentage of our daily commodities' plastic products. In Mexico 7.6 millions of tons of plastic in 2012 were wasted, which low density polyethylene LDPE, and high density polyethylene HDPE were the most abundant. Increasing cost, and decreasing space of landfills are forcing considerations of alternative options for PSW disposal. Years of research, study and testing have resulted in a number of treatment, recycling and recovery methods for plastics that can be economically, and environmentally viable. The following work studies the possibilities of polyethylene recycling. Nowadays, non-catalytic thermal cracking (Pyrolysis) is receiving renewed attention, due to the fact of added value on a crude oil barrel and its very valuable yielded products, but a fact remains that advanced thermo-chemical recycling of polyolefin still lacks the proper design, and kinetic background to target certain desired products and/or chemicals. On the other hand some research have shown a good performance that can be used in a real plant. ASPEN Plus is used to simulate a non-catalytic thermal cracking process. The process behavior of simulation is similar to the experimental data from other authors. Using gibbs free energy to identify the chemical equilibrium in system, its global minimization allows identifying the amount of substances present in the process. The simulation results demonstrate that it could be produced 49 % and 34 % wt of ethylene and propylene respectively from gas yield at 850 °C. Then scale the plant to produce ethylene and propylene from the pyrolysis and ethanol from a direct hydration of ethylene. Aspen Process Economics Analyzer is used in order to find the feasibility of the pyrolysis and ethanol production. The total sales/total production cost ratio obtained for the integrated process approaches was 2.55.

Keywords: ASPEN, pyrolysis, polyethylene, ethylene, propylene, ethanol

***Corresponding author: A. J. Castro Montoya,** Facultad de Ingeniería Química, División de Estudios de Posgrado de Ciencias en Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo Gral. Francisco J. Mugica S/N, Ciudad Universitaria, 58030 Morelia, Michoacán, Mexico, E-mail: ajcastro@umich.mx
A. Vargas Santillán, J. C. Farias Sanchez, M. G. Pineda Pimentel, Facultad de Ingeniería Química, División de Estudios de Posgrado de Ciencias en Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo Gral. Francisco J. Mugica S/N, Ciudad Universitaria, 58030 Morelia, Michoacán, Mexico

1 Introduction

Polyethylene (PE) have excelled among many other materials due to its properties, such polymer is used as containers for different products, mainly in food, agricultural, construction, textile, automotive among others. Plastics have accelerated their output by continuously adding new products to be emerging in market. China leads world production with 15 % of all world plastic followed by Germany with 7 %; Mexico produces only 2% of the 241 million tons produced globally. Figure 1 shows the production of plastics worldwide (Plasticseurope 2013).

The Plastic products industry is important in Mexico since nationwide is to 3.6 % of gross domestic product manufacturing (GDP). About 5.2 million ton were consumed in 2012, of which for its chemical, thermal and mechanical properties, the high density polyethylene (HDPE) and low density polyethylene (LDPE) were the most used (Conde Ortiz 2013).

At 2013, NOM-161-SEMARNAT-2011, was published in Mexico establishing some criteria for classify PSW and other wastes that are generated in high level. In that year, 4.2 million tons of plastic were discarded and only 11 % were recycled to produce plastics again, 2 % were used for energy recovery, discarding more than 3.6 million tons of plastic waste.

It has to be analyzed which can be an alternative in the reuse of waste sources, that can replace fossil and agricultural sources. In this sense it is necessary to propose methods for recycling or reuse plastics generated by different products.

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Experimental study of the production of high purity ethanol using a semi-continuous extractive batch dividing wall distillation column

Ulises Miguel García-Ventura[a], Fabricio Omar Barroso-Muñoz[a], Salvador Hernández[a,*], Agustín Jaime Castro-Montoya[b]

[a] Universidad de Guanajuato, Campus Guanajuato, DCNyE, Departamento de Ingeniería Química, Noria Alta s/n, Guanajuato, Gto., 36050, Mexico
[b] Universidad Michoacana de San Nicolás de Hidalgo, Facultad de Ingeniería Química, Ciudad Universitaria, Col. Felicitas del Río, 58060, Morelia, Michoacán, Mexico

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ABSTRACT

In this paper, the production of high purity ethanol using an experimental dividing wall distillation column using glycerol as entrainer is studied considering batch and semi-continuous operations. In the semi-continuous distillation, an ethanol–water mixture of composition 92% wt. ethanol was introduced in the pot and the glycerol was supplied through a continuous feed near to the top of the distillation column, it was possible to produce a distillate with a composition higher than 99% wt. ethanol. This result is important since it is possible to use this ethanol mixed with gasoline in the current motor vehicles operated with gasoline.

1. Introduction

Despite the process used to obtain bioethanol, a diluted stream of bioethanol is obtained (around 10% wt. of ethanol) and fed to a process separation in order to recover the bioethanol [1]. Several methods have been used to obtain high purity bioethanol, usually a first conventional distillation column is used to remove the water as bottoms product and the distillate contains most of the bioethanol [2]. This first distillation column plays an important role since as the distillate reaches the azeotrope composition of ethanol-water the energy required in the reboiler increases exponentially, thus a negative net energy gain can be obtained in the cycle of production of bioethanol. For that reason, the composition reached in this distillation column is really important as explained in the work of Kiss et al. [1]. In order to obtain high purity bioethanol the preferred industrial method is the extractive distillation using several entrainers; for instance, ethylene glycol, glycerol, ionic liquids and others [3]. From an economic point of view, the glycerol is the cheapest and is obtained as a side product in the production of biodiesel.

This extractive distillation process can be improved by using a dividing wall distillation (DWDC) that can save both energy and capital costs [4]. The DWDC is thermodynamically equivalent to the Petlyuk distillation column when no heat transfer occurs through the wall (Fig. 1). Both complex distillation columns can be used for the separation of a ternary mixture (ABC), where component A is obtained as top product, component B as side stream and component C as bottoms products.

It has been proven the effective use of DWDCs in the purification of bioethanol [5], reactive distillation to produce biodiesel and esterification reactions [6], but most of the studies have been carried out using process simulators, so that the main contribution of this paper is in the experimental production of high purity bioethanol using a DWDC and glycerol as entrainer since the use of ethylene glycol can be forbidden in the near future due to its toxicity [7]. It is important to highlight that in those applications, authors have reported energy savings of around 30% in contrast to the conventional distillation sequences. For that reason, we are interested in using DWDCs in the purification of bioethanol using glycerol, since distillation and dehydration can represent up to 37% of the total energy involved in the cycle of production of bioethanol [2]. Then, the reduction of the energy required in the purification stage is an important opportunity to improve the whole process of production of bioethanol.

2. Details of the experimental DWDC

We have designed, implemented and operated a DWDC that consists of three packed sections of Teflon™ Raschig rings, the sections are numbered from the pot to the condenser (see Fig. 2),

* Corresponding author.
E-mail addresses: hernasa@ugto.mx, hernasa@me.com (S. Hernández).

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Financial Risk Assessment and Optimal Planning of Biofuels Supply Chains under Uncertainty

José Ezequiel Santibañez-Aguilar[1] · Gonzalo Guillen-Gosálbez[2,3] · Ricardo Morales-Rodriguez[4] · Laureano Jiménez-Esteller[3] · Agustín Jaime Castro-Montoya[1] · José María Ponce-Ortega[1]

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Abstract Biofuels provide an attractive alternative for satisfying energy demands in a more sustainable way than fossil fuels. To establish a biorefinery, an optimal plan must be implemented for the entire associated supply chain, covering such aspects as selection of feedstocks, location, and capacity of biorefineries, selection of processing technologies, production amounts and transportation flows. In this context, there are several parameters, including the availability of biomass, product demand, and product prices, which are difficult to predict because they might change drastically over the different seasons of the year as well as across years. To address this challenge, this work presents a mathematical programming model for the optimal planning of a distributed system of biorefineries that considers explicitly the uncertainty associated with the supply chain operation as well as the associated risk. The potential of the proposed approach is demonstrated through its application to the production of biofuels in Mexico, considering multiple raw materials and products.

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✉ José María Ponce-Ortega
jmponce@umich.mx

1 Chemical Engineering Department, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Michoacán 58060, Mexico

2 Centre for Process System Engineering (CPSE), Imperial College London, London SW7 7AZ, UK

3 Departament d'Enginyeria Quimica, Universitat Rovira i Virgili, Av. Països Catalans 26, Tarragona 43007, Spain

4 Universidad de Guanajuato, Guanajuato 36050, Mexico

Keywords Biorefineries · Biofuels · Optimization · Supply chains · Financial risk · Uncertainty

Introduction

In the recent past, biomass has gained considerable attention as feedstock for the production of several products, especially for energy production through biorefineries [1]. Biofuels can be produced from selected agricultural biomass, proving a sustainable and eco-friendly energy option [2]. The implementation of biorefineries requires the analysis of several aspects, especially the biomass yield on the farm and the fuel production in the biorefinery because these two factors are the most powerful in determining the efficacy of a biofuel production system [3]. Other important factors include feedstock selection, processing routes, products, harvesting sites, processing facilities, and markets, which can be addressed through the optimization of the corresponding supply chain [4]. According to Georgiadis et al. [5], most of the reported approaches for designing supply chains have addressed decisions about the location of new facilities, selection of technologies, feedstocks, products, and distribution of feedstocks and products. In the context of biorefineries, several works on supply chain design have been developed. This way, Van Dyken et al. [6] presented a mixed-integer linear programming model (MILP) for designing biomass-based supply chains. Natarajan et al. [7] developed a model to determine the optimal locations of processing plants for methanol production. Shabani and Sowlati [8] studied the supply chain configuration of a forest biomass power plant. Lin et al. [9] presented a supply chain optimization model to minimize the annual bioethanol production cost, simultaneously considering

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Production of Fermentable Sugars and Hydrogen-Rich Gas from *Agave tequilana* Biomass

Juan Carlos Farías-Sánchez [1] · Ulises Velázquez-Valadez [1] · Alfonso Vargas-Santillán [1] · María Guadalupe Pineda-Pimentel [1] · Erick Alejandro Mendoza-Chávez [1] · José Guadalupe Rutiaga-Quiñones [2] · Jaime Saucedo-Luna [1] · Agustín Jaime Castro-Montoya [1]

Published online: 6 October 2016

Abstract The Mexican tequila industry annually processes approximately 1×10^6 *Agave tequilana* plants, generating approximately 1.78×10^8 kg of bagasse per year. This biomass is considered an attractive alternative to fossil fuels as an energy source and to produce biofuels and/or chemical products because it is produced and used without adversely affecting the environment. The first aim of the present work was to determine the effect of temperature, the concentration of H_2SO_4, and reaction time on the hydrolysis of agave bagasse to maximize the fermentable sugars using a steam explosion. This step process generated 71.11 g/L of reducible sugars in the supernatant (59.29 % glucose, 29.05 % xylose, and 11.66 % fructose) and unconverted organic matter of enzymatic hydrolysis bagasse (35.4 % α-cellulose, 7.33 % hemicellulose, 49.91 % lignin, and 7.31 % ashes). A mathematical surface response analysis of the hydrolysis was used for process optimization. The second aim involves the study of the thermodynamics of the reforming of unconverted organic matter from enzymatic hydrolysis of *Agave tequilana* bagasse (ATB) evaluated by the Gibbs free energy minimization method for hydrogen production. The effect of the parameters on the system performance measures, such as reaction temperature (T), Water/Biomass ratio (WBR), and pressure (P), were also investigated. The maximum H_2 production obtained was 23.2 mol of H_2/271.5 g ATB with a WBR $\geq$ 11 and a temperature of 740 °C. These findings indicate that the temperature and WBR are essential factors in the production of H_2, which was reflected in the efficiency of the process.

Keywords Lignocellulose residue · Acid hydrolysis · *Agave tequilana* · Hydrogen · Thermodynamic analysis

Introduction

The energy sector is considered one of the most important because it contributes substantially to the national economy, stimulating essential factors for all productive activities, employment, and basic consumer goods. Globally, 88 % of the total energy consumption is produced from non-renewable sources, and only 12 % comes from renewable sources such as biogas, wind, geothermal, hydro, solar, and biomass [1], such is shown in Fig. 1.

A major challenge facing society today, due to exponential population growth in a very short time, the rapid and continuous reduction of deposits of fossil fuels and growing concern about the environmental effects of fossil fuel use, is to cover the increased demand for energy by identifying and developing alternative energy sources. In recent years, there has been more interest from the public and private sectors in exploring alternatives for power generation and other industrial products for consumption or export through biological processes and/or biomass resources.

Currently, in Mexico, there is a legal mandate to generate 35 % of electricity from non-fossil fuels in 2024 in order to promote the sustainability of the energy sector, increase energy security, and mitigate the negative impacts that the

✉ Agustín Jaime Castro-Montoya
ajcastro@umich.mx

[1] Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Av. Fco. J. Mújica S/N, Edificio V1, Ciudad Universitaria, Col. Felicitas del Rio, C.P. 58040 Morelia, Michoacan, Mexico

[2] Facultad de Ingeniería en Tecnología de la Madera, Universidad Michoacana de San Nicolás de Hidalgo, Av. Fco. J. Mújica S/N, Edificio D, Ciudad Universitaria, Col. Felicitas del Rio, C.P. 58040 Morelia, Michoacán, Mexico