Computers and Chemical Engineering 34 (2010) 812–820

Contents lists available at ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

Separative reactors for integrated production of bioethanol and biodiesel

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ARTICLE INFO

Article history:
Received 24 July 2009
Received in revised form 7 September 2009
Accepted 10 September 2009
Available online 16 September 2009

Keywords:
Reactive distillation
Green catalysts
Solid acid/base
Sustainable biofuels
FFA
FAEE

ABSTRACT

Conventional integration of bioethanol and biodiesel plants employs the use of anhydrous ethanol in the biodiesel production process. The problem is that the production of anhydrous bioethanol is very energy-demanding, especially due to the azeotropic distillation required to producing high purity ethanol. The use of hydrous ethanol in the biodiesel production is preferable but unfeasible in conventional processes due to the equilibrium limitations and the economic penalties caused by the additional process steps. To solve this problem, this study proposes a novel energy-efficient integrated production of biodiesel from hydrous bioethanol. The key to success is a novel setup that combines the advantages of using solid catalysts with the integration of reaction and separation. This integrated process eliminates all typical catalyst-related operations, and efficiently uses the raw materials and the reactor volume in a separative reactor that allows significant savings in the capital and operating costs.

Rigorous simulations embedding experimental results were performed using computer aided process engineering tools – such as AspenTech Aspen Plus – to design the separative reactor and evaluate the overall technical feasibility of the process. The RD column was simulated using the rigorous RADFRAC unit with RateSep (rate-based) model, and explicitly considering three phases balances. Sensitivity analysis was used to determine the optimal range of the operating parameters. The main results are given for a plant producing 10 ktpy biodiesel (>99.9%wt) from hydrous bioethanol (96%wt) and waste vegetable oil with high free fatty acids content (∼100%), using solid acids as green catalysts.

1. Introduction

The governmental restrictions on discharge of green-house gasses associated with the steep changes in fossil fuel prices, shifted the worldwide trend to focus on renewable energy sources. Biodiesel is an alternative renewable fuel, currently produced from vegetable oils, animal fats or even recycled waste cooking-oils from the food industry (Buczek & Czepirski, 2004; Encinar, Gonzalez, & Rodriguez-Reinares, 2005; Kulkarni & Dalai, 2006). Compared to regular diesel, biodiesel is an environmental friendly fuel, with better combustion and reduced emissions of greenhouses gases, while sulfur is practically absent (Bowman, Hilligoss, Rasmussen, & Thomas, 2006). Due to its properties similar to regular diesel, biodiesel can be used in most modern diesel engines, in pure form or blended with petroleum diesel at any concentration (Balat & Balat, 2008).

Fatty esters, the main components of biodiesel, are currently produced by (trans-)esterification of tri-glycerides and free fatty acids, followed by several neutralization and purification steps. However, most traditional methods suffer from drawbacks related to the use of liquid acid/base catalysts, leading to major economical and environmental penalties (Knothe, Gerpen, & Krahl, 2005; Narasimharao, Lee, & Wilson, 2007). In spite of the technical problems (Meher, Vidya Sagar, & Naik, 2006), as well as the social and sustainability issues (Kumar & Sharma, 2005; Puhan, Vedaraman, Rambrahamam, & Nagarajan, 2005), the biodiesel production rate maintained a tremendous increase during the past ten years, mostly in Asia, US, and Western Europe—as illustrated by Fig. 1.

Although, biodiesel consists typically of fatty acid methyl esters – as methanol is the cheapest alcohol used at industrial scale – other alcohols such as ethanol may be employed as well. Bioethanol is the most important biofuel today, currently produced by fermentation of sugar derived from various crops such as sugar cane, corn and sugar beet (Kamm, Gruber, & Kamm, 2006; Liu & Tanaka, 2006; Mielenz, 2001; Solomon, Barnes, & Halvorsen, 2007). Just as other biofuels, ethanol can be blended with gasoline and used in existing or optimized flexi-fuel engines. Moreover, it burns cleaner than gasoline, producing less CO, CO_2 and NO_x emissions (Blottnitz & Curran, 2007). Fig. 2 shows that bioethanol is also experiencing a very fast growth on the global scale, particularly in Brazil and United States. Remarkably, Brazil gets more than 30% of its transport fuels from sugar cane bioethanol (SRI Consulting, 2009).

The production of anhydrous bioethanol is very energy-demanding – a major reason being the azeotropic distillation

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doi:10.1016/j.compchemeng.2009.09.005

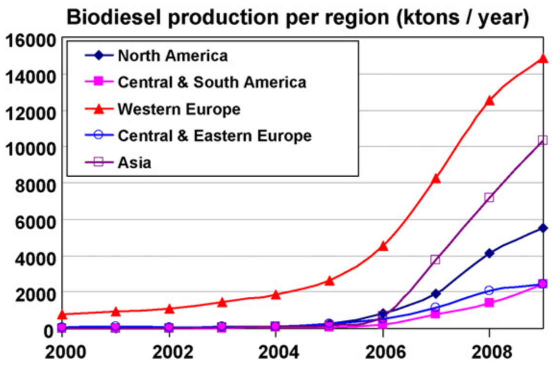

Fig. 1. Biodiesel production worldwide, per region.

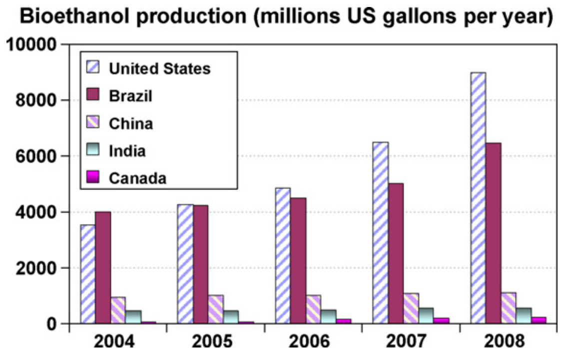

Fig. 2. Bioethanol production per country—Top 5.

required to producing pure ethanol – hence various process integrations were proposed in order to reduce the energy requirements (Cardona & Sanchez, 2007; Pfeffer, Wukovits, Beckmann, & Friedl, 2007). Since bioethanol can be used in the biodiesel production, many bioethanol plants integrate nowadays biodiesel production. According to SRI Consulting (2009), such an integrated bioethanol and biodiesel plant was developed by Dedini and it is being used since 2006 by Barralcool Mill (State of Mato Grosso, Brazil). Fig. 3 illustrates the current bioethanol–biodiesel process integration as well as the new model proposed in this work. Obviously, it would be much more convenient to use hydrous ethanol in the biodiesel production, but this is currently unfeasible in conventional processes due to equilibrium limitations and economic penalties caused by the additional processing steps.

This study makes a brief overview of existing biodiesel production processes and the associated benefits and drawbacks, and proposes a novel separative reactor using hydrous bioethanol over solid acid catalysts. This integrated solution simplifies the overall process and brings significant benefits, such as: high conversion and selectivity, elimination of conventional catalyst-related operations, no waste streams, as well as reduced capital and operating expenditures. The process design of a fatty acid ethyl esters plant described here is based on experimental results, integrated in rigorous simulations performed using AspenTech Aspen Plus as a computer aided process engineering tool (Aspen Technology, 2009a, 2009b).

2. Biodiesel production processes

Nowadays, the most widespread manufacturing technologies use homogeneous catalysts, in batch or continuous processes where both reaction and separation steps can create bottlenecks. The literature study reveals the following processes currently in use at pilot or industrial scale:

1. *Batch processes*. These allow high flexibility with respect to composition of the feedstock. The trans-esterification is performed using an acid or base catalyst (Lotero et al., 2005; Narasimharao et al., 2007). Nevertheless, the equipment productivity is low and the operating costs are high (Van Gerpen, 2005). Moreover, the use of liquid catalyst has severe economical and environmental penalties (Hanna, Isom, & Campbell, 2005).
2. *Continuous processes* combine the esterification and trans-esterification steps, allowing higher productivity. However, most of these processes are still plagued by the disadvantages of using homogeneous catalysts (Vicente, Martinez, & Aracil, 2004) although solid catalysts emerged in the last decade (Dale, 2003; Dossin, Reyniers, Berger, & Marin, 2006; Kiss, Dimian, & Rothenberg, 2006a; Kiss, Dimian, & Rothenberg, 2006b; Kiss, Rothenberg, Dimian, & Omota, 2006). Nevertheless, integrated processes based on reactive distillation have been also reported (He, Singh, & Thompson, 2006; Kiss, Dimian, et al., 2006a, 2006b; Kiss, Rothenberg, et al., 2006; Suwannakarn, Lotero, Ngaosuwan, & Goodwin, 2009). Moreover, an innovative process – known as ESTERFIP-H$^{\text{TM}}$ – was developed for the trans-esterification with methanol by the French Institute of Petroleum. The process is based on heterogeneous catalyst based on zinc and aluminum oxides and it is currently being applied in commercial plants (Bournay, Casanave, Delfort, Hillion, & Chodorge, 2005). However, it requires relatively high temperature (210–250 °C) and pressure (30–50 bar).
3. *Supercritical processes* were developed to solve the problem of miscibility of oil and alcohol that hinders the kinetics of trans-esterification, as well as to take advantage of not using a catalyst at all. However, the operating conditions are severe ($T > 240\,^{\circ}\mathrm{C}$, $p > 80$ bar) and therefore require special equipment (Cao, Han, & Zhang, 2005; He, Wang, & Zhu, 2007).
4. *Hydrolysis and esterification processes*. These are simpler processes as the glycerides are hydrolyzed first to fatty acids that are esterified in a second step to fatty esters (Kusdiana & Saka, 2004; Minami & Saka, 2006). Such processes have become very

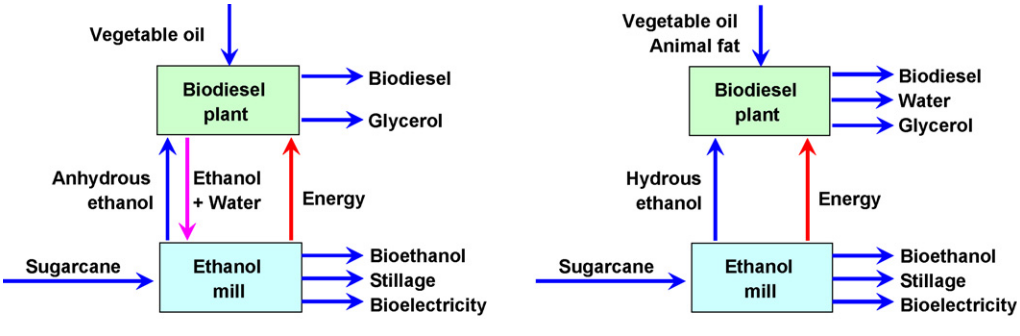

Fig. 3. Integrated bioethanol–biodiesel plant: present (left) and future (right).