Bioresource Technology 101 (2010) 5266–5274

Contents lists available at ScienceDirect

Bioresource Technology

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

Process simulation and economical evaluation of enzymatic biodiesel production plant

Lene Fjerbaek Sotoft *, Ben-Guang Rong, Knud V. Christensen, Birgir Norddahl

Institute of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark

ARTICLE INFO

Article history:
Received 27 November 2009
Received in revised form 25 January 2010
Accepted 26 January 2010
Available online 19 February 2010

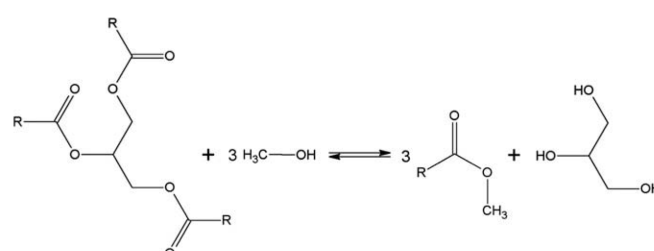
Keywords:
Enzyme
Biodiesel
Process simulation
Process design
Process economy

ABSTRACT

Process simulation and economical evaluation of an enzymatic biodiesel production plant has been carried out. Enzymatic biodiesel production from high quality rapeseed oil and methanol has been investigated for solvent free and cosolvent production processes. Several scenarios have been investigated with different production scales (8 and 200 mio. kg biodiesel/year) and enzyme price. The cosolvent production process is found to be most expensive and is not a viable choice, while the solvent free process is viable for the larger scale production of 200 mio. kg biodiesel/year with the current enzyme price. With the suggested enzyme price of the future, both the small and large scale solvent free production proved viable. The product price was estimated to be 0.73–1.49€/kg biodiesel with the current enzyme price and 0.05–0.75€/kg with the enzyme price of the future for solvent free process.

1. Introduction

The major operation in biodiesel production that decides the process route is the transesterification of the vegetable oil or animal fat into fatty acid methyl esters (FAME), the primary product. Typically methanol is used for the transesterification producing methyl esters and glycerin as byproduct (see Eq. (1)). This reaction can be carried out by various forms of catalysts, but so far industrially only chemical homogeneous catalysts are used in large scale. Smaller pilot plants with enzymatic catalysts are reported, but not to a very large scale (Du et al., 2008). In order to evaluate the potential and remaining obstacles of introducing enzymes as the preferred industrial catalyst, analysis of economical as well as environmental impacts of the alternative processes must be evaluated compared to the conventional process. The economy of the traditional production method has been thoroughly analyzed as by Haas et al. (2006), though the raw material price has increased since the publication of Haas et al. (2006). The raw material price based on 0.52 US$/kg soybean oil accounted for 88% of the production costs in a 37.900 m^3 biodiesel/year continuous production plant (Haas et al., 2006).



(1)

The industrial production of biodiesel has had a very turbulent lifetime due to the changes in prices of raw materials and fossil fuels as well as regulatory changes and production capacity of biodiesel. All of this affects the process economy on a global scale. When looking at the sustainability of producing biodiesel, this has been questioned in particular with respect to virgin oils as raw materials (Reijnders and Huijbregts, 2008). Nevertheless, if biodiesel is to be produced, an industrial process must be able to produce a product that meets the specifications, i.e., for Europe (EN 14214, 2008).

Traditional homogeneous and alternative heterogeneous chemical catalysts and supercritical conditions have been evaluated with regard to process economy for a continuous and batch processes (Table 1). Batch process evaluation has also been carried out by Sakai et al. (2009) and Noordam and Withers (1996) including homogeneous and heterogeneous chemical catalysts and various

* Corresponding author. Tel.: +45 6550 7443; fax: +45 6550 7354.
E-mail address: lfj@kbm.sdu.dk (L.F. Sotoft).

0960-8524/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2010.01.130

Table 1
Comparison of previous studies of process economy of biodiesel production.

	Production size (mio. kg/year)	Operation mode	Raw material	Glycerol sales included	Product price (€/kg)
Sakai et al. (2009)	7.26	Batch	Waste cooking oil	No	0.18–0.19
Noordam and Withers (1996)[a]	7.8	Batch	Canola oil	Yes	0.55
Marchetti and Errazu (2008)	36.04	Continuous	Waste cooking oil	Yes	0.32–0.33
West et al. (2008)	8	Continuous	Waste cooking oil	Yes	0.14
Zhang et al. (2003b)	8	Continuous	Waste cooking oil	Yes	0.46
Nelson et al. (1994)	100	Continuous	Beef tallow	Yes	0.25
Bender (1999)	101.20	Continuous	Animal fats	Yes	0.26
You et al. (2008)	8–100	Continuous	Soybean oil	Yes	0.49–0.62
Haas et al. (2006)	33.31	Continuous	Soybean oil	Yes	0.38
Zhang et al. (2003b)	8	Continuous	Virgin vegetable oil	Yes	0.62
Bender (1999)	1.76	Continuous	Canola oil	Yes	0.33
Santana et al. (in press)	10.5	Continuous	Castor oil	Yes	1.56
van Kasteren and Nisworo (2007)[a]	8–125	Continuous	Waste cooking oil	Yes	0.15
West et al. (2008)[a]	8	Continuous	Waste cooking oil	Yes	0.66

[a] Supercritical process, no other catalysts.

production ranges as well as two different product purification methods. Batch processes are only relevant compared with existing batch processing plants' economy, since if biodiesel is to be produced viable as a ''true'' bulk chemical then continuous operation is the only realistic option (Seider et al., 2004). Super critical conditions eliminate the need of catalyst and increase reaction rate (Saka and Kusdiana, 2001), but is a very costly production method.

For continuous processes, the prices for produced biodiesel were 0.14–0.46 and 0.33–0.62€/kg when using waste cooking oils, etc. and virgin vegetable oils, respectively (see Table 1). Batch production has been estimated to give biodiesel at 0.18–0.19 and 0.55€/kg for waste cooking oil and canola oil, respectively (see Table 1). This is for as well homogeneously as heterogeneously catalyzed processes. Most studies include a glycerol credit with a price/kg glycerol depending on the quality of the glycerol. Therefore, this study also includes this for comparative purposes.

Several processes of theoretical industrial scales have been simulated, but generally lack incorporation of realistic data and actual industrial performance for mass and energy balances. Therefore, some of the simulation results, i.e., water consumption and waste fractions are unrealistically low. As an example, Zhang et al. (2003a) have done a simulation work for four cases, including alkaline catalysis with NaOH of virgin oils and waste cooking oil as well as acid catalysis with either traditional water washing or hexane extraction of methyl esters. The simulation included a liquid–liquid extraction (water washing) of about 1177.20 kg/h biodiesel with 11 kg/h of water, which seems an unrealistic ratio of water to biodiesel when compared to real industrial unit operation in biodiesel production. Waste water from a biodiesel production can be as much as 47.5 kg for production of 100 kg biodiesel (Daka Biodiesel, 2009). The former simulation results leads to an underestimation of the total water consumption. A more realistic mass ratio of water to oil of 1:1 is, i.e., used by Santana et al. (in press) for a process catalyzed by NaOH with castor oil and ethanol as raw materials. The latter simulation gives more reliable results with respect to water consumption and liquid–liquid extractor size and price.

Some industrial processes use KOH as catalyst instead of NaOH. Where the cheaper NaOH gives water soluble salts after neutralization with acid, the more expensive KOH gives a precipitate of potassium sulphate and phosphate when neutralizing with sulphuric and phosphoric acid, respectively. The precipitation of salts reduces the total water consumption, because the water can be recirculated to an extent which is impossible when using NaOH. The precipitated salt can furthermore be sold as fertilizer. This is the technology used industrially by BDI – Biodiesel International. Only the use of KOH as by BDI can justify low total water consumption for the whole process due to water recycle, while the use of NaOH (as by Zhang et al. (2003a)) as a catalyst cannot. In both cases, the water consumption of the liquid–liquid extraction step isolated is of the same magnitude, but the potential water for recycling is very different.

None of the references in Table 1 involves biodiesel production catalyzed by enzymes. Enzymes are more expensive and slower reacting than traditional chemical catalysts, but give a much easier and simpler biodiesel purification. A life cycle comparison including biocatalysts has been carried out by Harding et al. (2008), but the analysis need optimization on several points. Water washing is not needed when using enzymes, but still included in the study. The washing step is only used when chemical salt catalyst residues, i.e., sodium ions, must be removed from the biodiesel. This is therefore a redundant step when using enzymes.

The prospect of the present paper is to bring biodiesel production with enzymes as catalysts closer to industrial scale application and elucidate the main obstacles that need to be solved for the process to be economically and environmentally sustainable.

Therefore, the paper evaluates several important and highly relevant scenarios for enzyme catalyzed biodiesel production processes. Simulations with methanol and solvent-free/co-solvent operations are carried out to investigate how this affect enzyme performance and process design and to elucidate what effect this has on the process economy. That is, too high concentrations of methanol inhibit the enzymes and reduce their lifetime. Therefore, optimal feeding of the methanol is crucial within the process. The process must be operated with maximum 1 mol methanol per

Table 2
Scenarios and data used for process simulation.

Scenario	1	2	3	4
Alcohol	Methanol	Methanol	Methanol	Methanol
Cosolvent	No	No	*tert*-Butanol	*tert*-Butanol
Enzyme price[a] (US$/kg)	1000/10 (762.71/7.627€)	1000/10	1000/10	1000/10
Data provided by	Shimada et al. (1999)	Shimada et al. (1999)	Li et al. (2006)	Li et al. (2006)
Productivity (Fjerbaek et al., 2009) (kg biodiesel/kg enzyme)[b]	1200	1200	4250	4250
Yield and reaction time	>96% and 48 h	>96% and 48 h	95% and 12 h	95% and 12 h
Production size (tons/year)	8000	200,000	8000	200,000

[a] The enzyme prices equal 762.71 and 7.627€/kg, respectively.
[b] Productivity calculated from 95% yield, 54 cycles and 4 wt.% enzyme out of reaction mixture.