Energy xxx (2014) 1–15

Contents lists available at ScienceDirect

Energy

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

Process intensification in biodiesel production with energy reduction by pinch analysis

Valentin Pleşu [b], Joan Subirana Puigcasas [a], Guillem Benet Surroca [a], Jordi Bonet [a, b], Alexandra E. Bonet Ruiz [a, b, *], Alexandru Tuluc [b], Joan Llorens [a]

[a] University of Barcelona, Department of Chemical Engineering, 1, Martí i Franquès Street, E-08028 Barcelona, Spain
[b] University POLITEHNICA of Bucharest, Centre for Technology Transfer in Process Industries (CTTPI), 1, Gh. Polizu Street, RO-011061 Bucharest, Romania

ARTICLE INFO

Article history:
Received 28 January 2014
Received in revised form
30 October 2014
Accepted 5 November 2014
Available online xxx

Keywords:
Energy efficiency
Energy conservation
Heat engine
Pinch analysis
Short chain fatty acids
Biodiesel additives

ABSTRACT

The overall process of biodiesel synthesis from vegetable oil and methanol is spontaneous according to Gibbs energy values. Therefore, a classical process scheme consisting of reactor followed by distillation columns train is grouped in a single hybrid reactive extraction column. Minimum energy consumption is calculated using Pinch Analysis, taking into account the minimum energy thermodynamically required by process units, e.g. distillation. Process Integration decreases dramatically the minimum energy requirements. Using Pinch Analysis, a useful tool is provided to calculate the minimum energy requirements of alternative processes, the effect of inclusion of the distillation column is to be underlined.

The intensified process provides biodiesel and glycerol valorisation with very low energy consumption. A conceptual design of hybrid reactive extraction column useful for several input oils and fats is proposed, considering first pure triglycerides as raw materials and then complex mixtures of triglycerides as in real oil compositions.

1. Introduction

Biodiesel is one of the main products of the European biorefineries. In European Union, Directive 2009/28/EC require that every year the production of biofuels increases with the aim that by 2020, 10% of transportation fuels to be biofuels. Most of the UE car engines are diesel and therefore biodiesel plays a crucial role. The classical scheme to produce biodiesel including a reactor followed by a train of distillation columns to purify the products and to recover non-reacted methanol, requires a high-energy demand [1]. Great improvements on biodiesel process are required to compete with the mature petro-diesel process. Combining in the same unit reaction and separation as a technique of process intensification proved to be an effective way to reduce the energy requirements for many processes. Gibbs energy provides a valuable guide to identify when process intensification is advantageous. In case of biodiesel synthesis, the overall intensified process does not require energy consumption [2]. The transesterification of vegetable oil with methanol is thermodynamically spontaneous unlike mixing. The temperature and excess of methanol are more useful to favour phase mixing than to displace the reaction equilibrium towards biodiesel formation [3]. This statement is in agreement with experimental results, when mixing is produced by ultrasounds [4], or in supercritical conditions [5], or when using reactors that provide an intensive mixing [6]. All these techniques require an excess of methanol. Our research team has recently proposed a novel overall intensified process for triolein transesterification without the need of methanol excess, using a hybrid reactive extraction column that produces pure biodiesel and glycerol [7]. Both reactants flow in counter-current, which is more efficient than other flow configurations such as cross-flow [8]. Methanol is partially soluble in FAME (fatty acid methyl ester) [9], consequently can be recovered in the non-reactive section, using glycerol as extractive agent. Without the use of the non-reactive section, an excess of methanol is required [10]. The capital costs and risks become lower as the number of process units decreases due to the intensification [11].

Several oils can be used as raw material for biodiesel: waste vegetable cooking oils [12], algae oil [13], fish oil [14], *Sapindus mukorossi* kernel oil [15], Canola or Camelina oil [16], Karanja [17],

* Corresponding author. University POLITEHNICA of Bucharest, Centre for Technology Transfer in Process Industries (CTTPI), 1, Gh. Polizu Street, RO-011061 Bucharest, Romania. Tel.: +40 21 4023916; fax: +40 21 3185900.
E-mail address: a_bonet@chim.upb.ro (A.E. Bonet Ruiz).

http://dx.doi.org/10.1016/j.energy.2014.11.013
0360-5442/

Table 1
Some biodiesel compositions limited by legislation.

% wt	EN 14214	ASTM D6751-08
Ester	>96.5	
Water	<500 mg/kg	<0.05% vol
Impurities	<24 mg/kg	
Linolenic methyl ester	<12	
Methanol	<0.2	<0.2
Monoglycerides	<0.8	
Diglycerides	<0.2	
Triglycerides	<0.2	
Free Glycerine	<0.02	<0.02
Total Glycerine	<0.25	<0.24

rubber seeds oil [18], castor oil [19], etc. Algae oil is considered a good oil source for biodiesel. To produce 50% of the fuel required in USA, an agriculture area equivalent to 24% of the USA fields should be dedicated to palm oil production meanwhile only 3% would be required using microalgae [20]. Algae oil can be collected with low energy requirements by CO_2 media acidification, low-power pulsed electromagnetic field and static mixer turbulences to break the membrane and posterior decantation to separate oil, water and cellular membranes [21]. However, palm oil is used as base case in Aspen Plus® documentation providing the composition of palm oil. The catalyst considered in the Aspen Plus® example is homogeneous. However, important advances are reported in literature concerning application of heterogeneous catalysts, e.g. Mg–Zn mixed metal oxide catalysts [22], acidic ionic liquid immobilized on poly divinylbenzene [23], hydrotalcite as basic catalyst [24] or sugar catalyst [8]. Furthermore, it is evaluated the suitability of the hybrid reactive extraction column for several pure triglycerides, fat and oils. The number of required reactive and non-reactive stages required for a hybrid extraction column able to treat several kinds of oils and fats is also determined. The UE and USA legislation related to biodiesel composition is taken into account (Table 1). The effect of presence of free fatty acids, as well as the potential for glycerol revalorization is not the scope of the present study. This allows providing more details about the biodiesel synthesis. The study focuses on aspects such as comparison between classical and intensified process for biodiesel synthesis from minimum energy point of view.

When alternative processes are available, the process with lower energy requirements, typically, is more efficient and preferable because it provides lower operation costs, higher energy conservation and lower environmental impact. However, the energy requirements comparison between processes is not an easy task because it depends on how well it is optimized and how process integration is made. The minimum energy consumption

Table 2
Palm oil feed composition.

Compound	AspenPlus® identifier	*x* (Mass)
Trioleine	OOO	0.0440
Trimirystine	MMM	0.0042
Tripalmitine	PPP	0.0551
Dipalmitine stearine	PPS	0.0106
Dipalmitine oleine	PPO	0.2962
Palmitine oleine Stearine	POS	0.0490
Dimiristate palmitine	MMP	0.0170
Dipalmitine Linoleine	PPLI	0.0923
Palmitine Dioleine	POO	0.2326
Palmitine Linoleine Oleine	PLIO	0.0968
Dioleine Stearine	OOS	0.0224
Dioleine Linoleine	OOLI	0.0058
Mirystine Palmitine Linoleine	MPLI	0.0220
1,3-Dipalmitine	PP	0.0520

Table 3
Mass percent of fatty acid for several kinds of oils.

FFA	*Jatropha curcas* oil	Algae oil		
		Tolypoghrix	Spirogyra	Spirulina
C 7:0				
C 8:0				
C 14:0		5.8	6.4	0.23
C 16:0	14.2	31.8	25.2	46.07
C 16:1		4.7	5.4	1.26
C 16:2		2.4	3.8	3.38
C 18:0	7.0	2.7	4.5	1.41
C 18:1	44.7	23.4	33.3	5.23
C 18:2	32.8	8.6	10.8	17.43
C18:3		8.4	0.7	8.87
Others	1.3	12.2	9.9	16.12

calculated with the aid of Pinch Analysis is a great stimulus to achieve efficient process conceptual designs. Although the methodology of taking into account the distillation column energy requirements in the Pinch Analysis was well established [25], the calculation of the minimum energy requirements of a distillation column, in a simple way, based on thermodynamic principles, was not described until recently [26]. The minimum energy requirement of a system is calculated taking into account the maximum heat exchangeable, fulfilling the second thermodynamic law and considering the distillation columns as heat engines that provide separation instead of work. At our knowledge, this approach to calculate the minimum energy requirements of a process has not been yet reported before in literature. This paper proposes to verify if classical process integration could compete with the proposed intensified process from energy point of view. In some cases, the energy savings for process intensification and the process integration are reported to be similar, e.g. the energy requirements for methanol and glycerol recovery can be decreased with 27% by using a divided wall column [27] or 23% with an appropriate heat exchange network [28].

Therefore, a comparison between the hybrid reactive extraction column and the classical scheme is required to verify the potential of the novel intensified process. The novel process is evaluated using several triglycerides and oils, i.e. to be close to real situations from this point of view.

2. Material and method

Biodiesel synthesis from palm oil using a classical process scheme available as example in AspenPlus® version 8.2 is used as base case, providing palm oil composition (Table 2). Thermodynamic data and kinetics are ready implemented in AspenPlus® v8.2

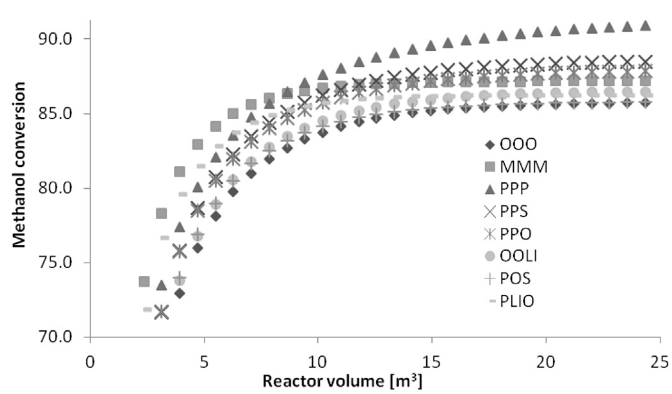

Fig. 1. Methanol and triglycerides reacting in co-current in a PFR.