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SCIENCE DIRECT
Catalysis Today 106 (2005) 193–196
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Pilot plant studies of biodiesel production using *Brassica carinata* as raw material

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Abstract

In recent years, the development of alternative fuels from renewable resources, like biomass, has received considerable attention. Biodiesel is defined as fatty acid methyl or ethyl esters from vegetable oils, when it is used as fuel in diesel engines and heating systems.

In this context, the cultivation of *Brassica carinata* as oilseed crop for biodiesel production in the south of Europe (Spain and Italy) and north of Africa has gained special interest, since it allows the use of set-aside lands, giving higher yields per hectare than the traditional Spanish crops.

Methyl or ethyl esters are the product of transesterification of vegetable oils with alcohol (methanol/ethanol) using an alkaline catalyst. In addition, the process yields glycerol, which has large applications in the pharmaceutical, food and plastics industries.

In the present work, the process of biodiesel production for pilot plant using *B. Carinata* oil as raw materials with methanol and using potassium hydroxide as catalyst has been studied.

The biodiesel quality meets European specifications defined by pr EN 14214:2002 (E). The obtained results have been used for industrial scale up of the process.

Keywords: Alternative fuels; Biodiesel; *Brassica carinata* oils; Fatty acid methyl esters; Pilot plant

1. Introduction

Diesel fuel plays an important role in the industrial economy of a country. This fuel runs a major part of the transport sector and their demand is increasing steadily, requiring an alternative fuel which is technically feasible, economically competitive, environmentally acceptable and readily available [1].

Biodiesel, which is synthesised by transesterification of vegetable oils or animal fats sources, is a realistic alternative of diesel fuel because it is produced from renewable resources and involves lower emissions than petroleum diesel [2]. In addition, it is biodegradable and contributes a minimal amount of net greenhouse gases or sulphur to the atmosphere. The transesterification process combines the oil with an alcohol. The most common form of biodiesel is made with methanol and vegetable oils in the presence of a suitable catalyst. Additionally, the process yields glycerol. *Brassica carinata*, a native plant of the Ethiopian Highlands widely used as food by the Ethiopians, has recently become object of increasing interest. This is due to its better agronomic performances in areas such as Spain, California and Italy that are characterised by unfavourable environmental conditions for the cultivation of *Brassica napus* (by far, the most common rapeseed cultivated in continental Europe). The agronomic performance and the energy balance described in other works [3] confirmed that B. carinata adapts better and is more productive both in adverse conditions (clay- and sandy-type soils and semi-arid temperature climate) and under low cropping system when it is compared with *B. napus*.

The objective of the present work was to study the process of biodiesel production at pilot plant scale using *B. carinata* oil as raw material with methanol and potassium hydroxide as catalyst.

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doi:10.1016/j.cattod.2005.07.163

2. Experimental

2.1. Materials

To produce biodiesel by base catalysed transesterification reaction. *B. carinata* oils were supplied by Koipe Spain. Free fatty acid content of the oil was determined according to AOCS Official Method CA 5a-40. The chemical properties of *B. carinata* oil are reported in Table 2. Certified methanol of 99.8% purity was supplied by Aroca (Madrid, Spain). The catalyst used was potassium hydroxide (90–92% purity) purchased from Merck.

2.2. Analytical method

2.2.1. Gas–liquid chromatography

Reaction products were monitored by capillary column gas chromatography, using a Hewlett-Packard 5890 Series II equipped with a flame ionisation detector (FID). The injection system was split-splitless. The carrier gas was helium at a flow rate of 1 ml/min, analysis operating conditions have been described in detail in a previous work. [4]. The internal patron technique has been used in order to quantify the amount of the chemical species.

2.2.2. Conventional analysis

The conventional analysis of biodiesel quality: acid value, iodine value, water content, density and viscosity were carried out using the methods developed by the Complutense University and compared with some of the biodiesel standard (The European Union Draft Standard prEN 14214).

3. Results and discussion

Preliminary studies in our laboratory using a factorial design of experiments procedure has been followed to optimize the variables that determine the yield of ester [5]. According to this study, the maximum yield of ester (98%) can be obtained, working with an initial catalyst concentration (1.5%), an operation temperature of (25 °C) and with an alcohol/oil molar ratio of (6:1). These models are useful to determine the optimum operating conditions for the industrial process using the minimal number of experiments with the consequent benefit from economical point of view. The used methodology (Factorial Design of Experiments, Statistical Analysis and Central Composite Design) allows to develop and to optimize this process, leading to obtain a simple technological model valid for the process scale up.

4. Pilot plant process and equipment

4.1. Biodiesel production and characterisation

Biodiesel was produced from 100 L of *B. carinata* oil in the pilot plant. A scheme of the main reaction unit is shown in Fig. 1. *B. carinata* oil is stored in a 1000 kg cone-bottom tank at room temperature. For the transesterification reaction, the oil is transferred to the main reaction tank. The main transesterification reaction was carried out in a completely stirred tank reactor (CSTR) of 200 L glass tank with a turbine agitator, under fixed pressure and temperature conditions. The reactor was also equipped with stationary

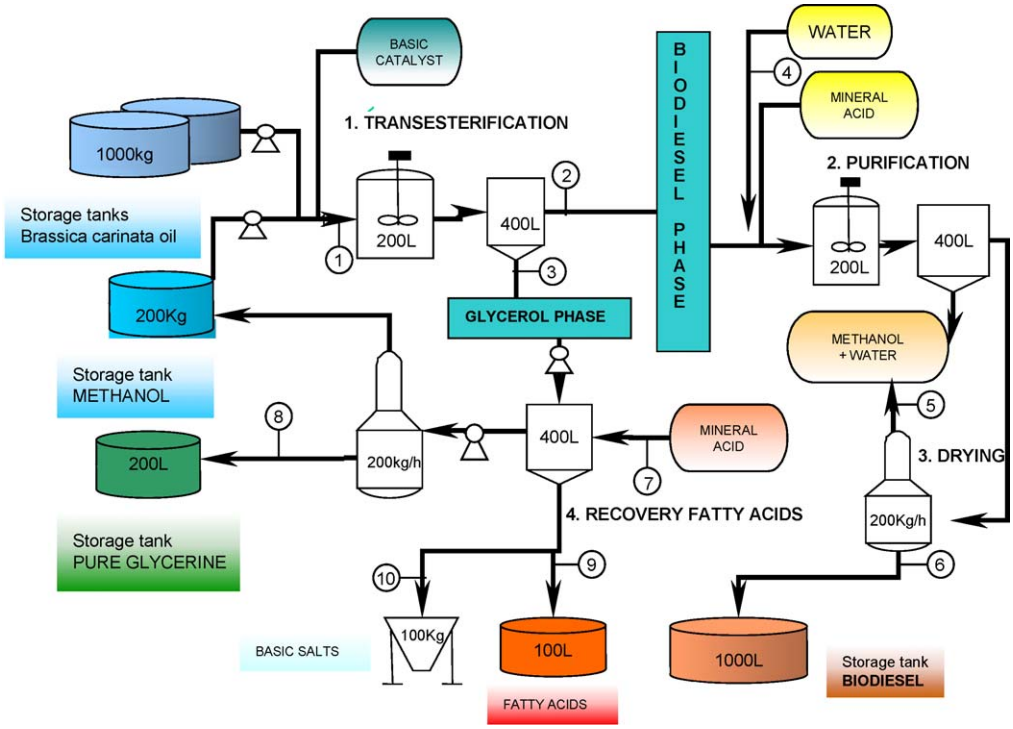

Fig. 1. Flow sheet of the transesterification process.

Table 1
Material balance of the process and yields obtained

	Stream										Yield (%)[a]
	1	2	3	4	5	6	7	8	9	10	
High erucic *B. carinata* oil (kg)	100										
Methanol (kg)	21.66	5.27	5.58		4.71	nd					
KOH (kg)	1.48		0.77		Traces	Traces					
Biodiesel kg)		97.65	0.05		0.15	97.03		0.05			0.98
Glycerol (kg)			12.34					10.39			0.10
Fatty acids (kg)	0.56	0.10				0.05			0.425		0.76[b]
Oils (kg)		1.54				1.28					
Soaps (kg)		0.05	0.26		0.05						
Water (kg)			0.05	38.91	38.91	Traces	1.08	1.28			
Phosphates (kg)										3.38	0.03
Phosphoric acid (kg)							3.07				
Total	123.7	104.61	19.05	38.91	43.82	98.36	4.15	11.72	4.25	3.38	

nd: not detected.
[a] Refering to *B. carinata* oil.
[b] Refering to the free fatty acids in the raw materials.

baffles attached along the surface. A load cell mounted on one leg of the reaction tank measures the reactant amounts. After preparing the alcohol solution with the catalyst, it is added to the reaction tank. The impeller speed was fixed at 0.02 Np. The reactants are agitated for 60 min and then the reaction mixture is transferred to a 400 L decanter for glycerine and methyl ester separation, allowing glycerol to separate by gravity for 2 h. Temperature, pressure and stirring speed controllers were provided.

4.1.1. Alcohol removal

Once glycerine and methyl ester phases have been separated, the excess alcohol in each phase is removed by flash evaporation, at 90 °C and 100 mmHg. The alcohol is recovered and is re-used. Care must be taken to ensure no water accumulates in the recovered alcohol stream.

4.1.2. Glycerine purification

Glycerine clean-up equipment is included in the pilot plant, so glycerine is obtained as a pure product. The glycerine by-product contains unused catalyst and soaps that are neutralised with an acid (phosphoric acid) and sent to a storage tank. The formed fatty acids were transferred to a storage container and the basic salt formed in this step is recovered and used as fertilizer.

4.1.3. Methyl ester wash

Once separated from the glycerine, the biodiesel is purified by washing gently with two volumes of water to remove residual catalyst, glycerol, methanol and soaps using a centrifuge, dried and sent to storage tank. The wash water temperature was set at room temperature.

4.2. The biodiesel purity and yield

In order to evaluate the biodiesel purity, the methyl ester concentration (wt.%) in the biodiesel phase was calculated. Conversely, to estimate the biodiesel yield after the reaction and separation stages, the biodiesel weight yield, relative to the initial amount of vegetable oil, was worked out.

Methyl ester concentration was nearly 100 wt.%. According to this result, the transesterification reaction was completed and, therefore, no difference in biodiesel purity was found after 1 h of reaction. However, if there are no side reactions, the biodiesel weight yields, relative to the initial amount of vegetable oil, should be nearly 100 wt.%. In this sense, two possible side reactions could occur, the triglyceride saponification or the free fatty acids of the vegetable oil neutralisation. Both of them produce potassium soap and, therefore, decrease the biodiesel yield. The free fatty acids neutralisation could not be substantial, since the acid index in the *B. carinata* oil was only 0.8 mg KOH g^{-1}. Consequently, triglyceride saponification must be the only possible side reaction. As shown in Table 1, a biodiesel yield of 97.03 wt.%, was obtained using potassium hydroxide as catalyst. This is due to the presence of the hydroxide group that originated soaps by triglyceride saponification. Owing to their polarity, the soaps dissolved into the glycerol phase during the separation stage after the reaction. In addition, the dissolved soaps increased the methyl ester solubility in the glycerol and this involved an additional loss of yield.

4.3. The material balance of the process

In order to quantify the yield loss, the process mass balance was determined analysing the methyl ester and glycerol phases. The mass balance of the process, relative to vegetable oil molar amount, includes the biodiesel molar yields and the molar yield losses produced by triglyceride saponification and methyl ester dissolution in the glycerol phase. The mass balance of the process and the products yield obtained are presented in Table 1. The methyl ester dissolution in the glycerol was only 0.05% after the reaction step.

Table 2
Quality control of (a) *Brassica carinata* oil and (b) biodiesel

Part (a)

Properties	*B. carinata* oil	AOCS official methods
Viscosity at 40 °C	55.07	ISO 3104
Density at 15 °C	0.879	Ca 10c-95
Water content (wt.%)	0.07	Ca 2e-84
Acid value (mg KOH g^{-1})	0.833	AOCS-Ca 5a-40
Iodine value (mg I_2 g^{-1})	109.4	AOCS-Cd 1d-92

Part (b)

Properties	*B. carinata* biodiesel	EU Draft standard PrEN 14214-2002
Viscosity at 40 °C	4.88	Maximum 5.00 mm^2/s
Density at 15 °C	810	Maximum 900 kg/m^3
Water content	300	Maximum 500 mg/kg
Biodiesel yield (wt.%)	97.10	Minimum 96.5% (m/m)
Monoglyceride content (wt.%)	0.8	Maximum 0.80% (m/m)
Diglyceride content (wt.%)	0.0	Maximum 0.20% (m/m)
Triglyceride content (wt.%)	0.0	Maximum 0.20% (m/m)
Free glycerol (wt.%)	0.01	Maximum 0.02% (m/m)
Total glycerol (wt.%)	0.12	Maximum 0.25% (m/m)
Acid value (mg KOH g^{-1})	0.06	Maximum 0.50 mg KOH g^{-1}r
Iodine value (mg I_2 g^{-1})	109.4	Maximum 120

4.4. Quality control of biodiesel

Some of the most important quality parameters of biodiesel (monoglyceride, diglyceride and triglyceride content: bonded, free and total glycerol levels; acid value and iodine value) are shown in Table 2. These parameters were compared with some of the biodiesel standards (The European Union Draft Standard, prEN 14214). The contents of individual glycerides (monoglycerides, diglycerides and triglycerides) were within the three specifications, which imply that the transesterification reaction was complete. Consequently, the bonded glycerol also met the specification parameter. Regarding to the free glycerol content, the measured values were lower than their parameter limits and this indicated that the glycerol residues were eliminated during the purification treatment. As the individual glyceride and free glycerol levels were under the specifications, the total glycerol content also met all the standards. The acid value is a measure of the fatty acid level in the biodiesel and depends on the free fatty acid content in the *B. carinata* oil and the transesterification process. The acid values were within specifications in all reactions.

Concerning the iodine value, it is a measure of the unsaturation level and, therefore, it only depends on the vegetable oil used as the raw material. In this sense, *B. carinata* oil has a relatively lower iodine values in comparison with other raw materials (e.g. sunflower oil) with a lower content of unsaturated fatty acids. For this reason, the measured iodine values were (109.4 mg I_2 g^{-1}). The iodine value was below the recent specified limit, 140, in the draft European Union Standards. The countries that first developed biodiesel in the European Union (e.g. Germany) utilised rapeseed oil as a raw material and therefore they included a lower specified limit for the iodine value (115 mg I_2 g^{-1}). The specified iodine value limit in the European Union draft standard was also initially 115 mg I_2 g^{-1}, but it has been changed recently to 120 mg I_2 g^{-1} to include a large range of raw materials. In fact, there is not a direct relation between the unsaturation level in the biodiesel and diesel engine malfunctioning. Nevertheless, the level of unsaturation is directly linked with the oxidation tendency. Consequently, in order to avoid oxidation, special precaution must be taken during the storage of biodiesel from vegetable oils.

5. Conclusion

The non-food use of *B. carinata* oil for biodiesel production was studied. Pilot plant studies of biodiesel, produced by transesterification of the oil extracted from the *B. carinata* seeds, displayed suitable physical–chemical properties for the use as diesel car fuel. These results make *B. carinata* as a promising oil feedstocks for biodiesel production. Its cultivation in coastal areas of (central–southern) Spain could offer the possibility of exploiting the Mediterranean marginal areas for energy purposes. The quality of biodiesel is in agreement with the European Specification defined by pr EN 14214:2002 (E). The results obtained, in this pilot plant, nearly to 98%, has been used for industrial scale up of this process.

Acknowledgment

Financial support from the (CICYT), Project PPQ 2002-03468, is gratefully acknowledged.

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