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New heterogeneous process for biodiesel production: A way to improve the quality and the value of the crude glycerin produced by biodiesel plants

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Abstract

With over 10 years of development and commercial use in Europe, biodiesel has now proved its value as a fuel for diesel engines. A sharp increase in the production of this kind of biofuel is expected in the near future. Biodiesel is obtained through transesterification reaction of vegetable oil by methanol. Several commercial processes to produce fatty acid methyl esters from vegetable oils have been developed and are available today. These processes use homogeneous basic catalysts such as caustic soda or sodium methylate which lead to waste products after neutralization with mineral acids. This paper provides a general description of a completely new continuous biodiesel production process, where the transesterification reaction is promoted by an heterogeneous catalyst. This process requires neither catalyst recovery nor aqueous treatment steps: the purification steps of products are then much more simplified and very high yields of methyl esters, close to the theoretical value, are obtained. Glycerin is directly produced with high purity levels (at least 98%) and is exempt from any salt contaminants. With all these features, this process can be considered as a green process.

Keywords: Biodiesel production; Transesterification; Vegetable oils; Heterogeneous catalysis; Glycerin

1. Introduction

The reactions for direct transformation of vegetable oils into methyl esters and glycerol have been known for more than a century. The reactions of interest today, mainly those producing methyl esters from rapeseed, soybean and sunflower oils, have been studied and optimized in order to manufacture the high quality diesel fuel known as biodiesel.

With over 10 years of commercial use in Europe, biodiesel has now proved its value as a fuel for diesel engines. [1–3]. The product is free of sulfur and aromatics, and, as it is obtained from renewable sources, it reduces the lifecycle of carbon dioxide emissions by almost 70% compared to conventional diesel fuel. Moreover, recent European regulations have restricted sulfur content in diesel fuel to no more than 50 wt. ppm in year 2005. Sulfur is known to provide diesel fuels with a lubricity that will disappear as the regulations take effect. Biodiesel addition at levels of 1–2% in diesel blends has the beneficial impact of restoring lubricity through an antiwear action on engine injection systems [4–5].

The biodiesel market is expected to grow rapidly to meet the new European Directive target of 5.75% volume biofuels in the transport sector by 2010.

Increasing biodiesel consumption requires optimized production processes allowing high production capacities, simplified operations, high yields, and the absence of special chemical requirements and waste streams.

Abbreviations: FAME, fatty acid methyl ester; MONG, matter organic non-glycerol

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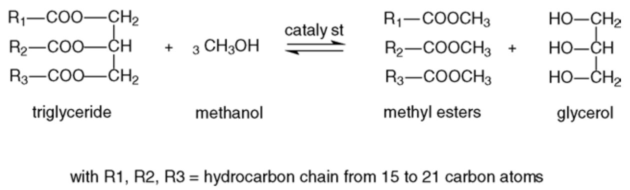

Fig. 1. Overall reaction for vegetable oils methanolysis.

2. Biodiesel production through transesterification

2.1. Transesterification reaction

The transesterification of triglycerides to fatty acid methyl esters (FAME) with methanol is a balanced and catalyzed reaction, as illustrated in Fig. 1. An excess of methanol is required to obtain a high degree of conversion.

The conventional catalysts in natural oil transesterification processes are selected among bases such as alkaline or alkaline earth hydroxides or alkoxides [6]. However, transesterification could also be performed using acid catalysts, such as hydrochloric, sulfuric and sulfonic acid, or using metallic base catalysts such as titanium alcoholates or oxides of tin, magnesium, or zinc. All these catalysts act as homogeneous catalysts and need to be removed from the products after the methanolysis step.

2.2. Conventional processes

Several commercial processes for FAME production have been developed. In conventional industrial biodiesel processes, vegetable oil methanolysis is achieved using a homogeneous catalyst system operated in either batch or continuous mode. Sodium hydroxide or sodium methylate is often used as catalyst. Sodium is recovered after the transesterification reaction as sodium glycerate, sodium methylate, and sodium soaps in the glycerol phase.

An acidic neutralization step with, for example, aqueous hydrochloric acid is required to neutralize these salts. In that case, glycerol is obtained as an aqueous solution containing sodium chloride. Depending on the process, the final glycerol purity is about 80–95%.

When sodium hydroxide is used as catalyst, side reactions forming sodium soaps generally occur. This type of reaction is also observed when sodium methylate is employed and traces of water are present. The sodium soaps are soluble in the glycerol phase and must be isolated after neutralization by decantation as fatty acids. The loss of esters converted to fatty acids can reach as high as 1% of the biodiesel production. These operations are illustrated in Fig. 2.

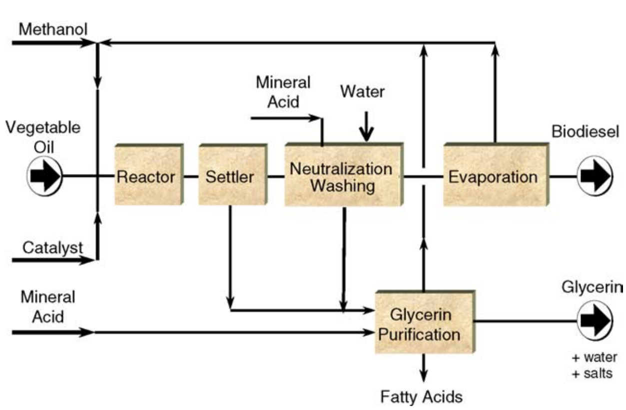

Fig. 2. Global scheme for a typical continuous homogeneous catalyzed process.

2.3. New heterogeneous catalyst process

Much effort has been expended on the search for solid acid or basic catalysts that could be used in a heterogeneous catalyzed process [7–10]. Some solid metal oxides such as those of tin, magnesium, and zinc are known catalysts but they actually act according to a homogeneous mechanism and end up as metal soaps or metal glycerates.

In this new continuous process, the transesterfication reaction is promoted by a completely heterogeneous catalyst. This catalyst consists of a mixed oxide of zinc and aluminium, which promotes the transesterification reaction without catalyst loss. The reaction is performed at higher temperature and pressure than homogeneous catalysis processes, with an excess of methanol. This excess is removed by vaporization and recycled to the process with fresh methanol.

The desired chemical conversion, required to produce biodiesel at the European specifications, is reached with two successive stages of reaction and glycerol separation in order to shift the equilibrium of methanolysis. The flow sheet of this process is presented in Fig. 3.

The catalyst section includes two fixed bed reactors, fed with vegetable oil and methanol at a given ratio. Excess of methanol is removed after each reactor by partial evaporation. Then, esters and glycerol are separated in a settler. Glycerol outputs are gathered and the residual methanol is removed by evaporation. In order to obtain biodiesel at the European specifications, the last traces of methanol and glycerol have to be removed. The purification section of

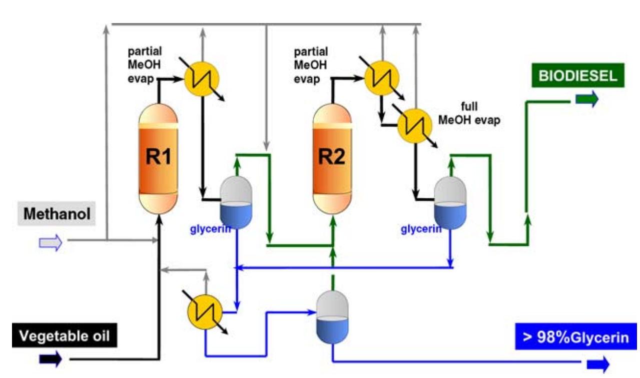

Fig. 3. Simplified flow sheet of the new heterogeneous process, Esterfif-H™.

Table 1
Main characteristics of biodiesel fuel obtained from rapeseed oil with heterogeneous catalyst

	Biodiesel from Reactor 1	Biodiesel from Reactor 2	European specifications
Weight composition (%)			
Methyl esters	94.1	98.3	>96.5
Monoglycerides	2.0	0.5	<0.8
Diglycerides	1.1	0.1	<0.2
Triglycerides	1.6	0.1	<0.2
Free glycerol	–	–	<0.02
Metal content (mg/kg)			
Group I (Na + K)	<2	<2	<5
Group II (Ca + Mg)	<2	<2	<5
Zn	<1	<1	–
Phosphorus content (mg/kg)	<10	<10	<10
Acid number (mg KOH/kg)	<0.3	<0.3	<0.5

methyl ester output coming from decanter 2 consists of a finishing methanol vaporization under vacuum followed by a final purification in an adsorber for removing the soluble glycerol.

3. Main characteristics of the products with heterogeneous process

Pilot plant experiments has been performed during the development of the new heterogeneous process. Biofuel and glycerin have been produced in the design industrial operating conditions and their main characteristics are given below.

3.1. Biodiesel fuels

The main characteristics of the biodiesel fuels produced from rapeseed oil with the heterogeneous catalyst are summarized in Table 1. Glycerides content and methyl esters content have been determined by gas chromatography using the European standard test methods (EN 14105/EN 14103).

3.2. Glycerin

The main characteristics of the glycerin co-produced with methyl esters from rapeseed oil with the heterogeneous catalyst are presented in Table 2. The glycerin obtained is limpid and colorless. The glycerol content of the glycerin produced is at least 98%. Neither ash, nor inorganic compounds are detected in the glycerin produced. The major impurities of the glycerin are water, methanol and matter organic non-glycerol (MONG, such as methyl ester).

Table 2
Main characteristics of glycerin obtained from rapeseed oil with heterogeneous catalyst

	Method	
Glycerol content (wt.%)	BS 5711-3	>98.0
Specific gravity 25 °C (kg/m^3)	ISO 3675	1264
Refractive index 20 °C	ASTM D1747	1.4735
Acidity (mg KOH/g)	EN 14104	0.1
Ash (wt.%)	ISO 6245	None
Chlorides (mg/kg)	EP5.0	<10
Chlorinated compounds (mg/kg)	EP5.0	<10
Halogenated compounds (mg/kg)	EP5.0	<10
Heavy metals (mg/kg)	ASTM D4951	None
Arsenic (mg/kg)	ISO 11969 D18	<0.1

4. Conclusions

Biodiesel is becoming a key component in the motor diesel pool, because of their attractive features. Increasing biodiesel consumption requires optimized production processes that are compatible with high production capacities and that feature simplified operations, high yields, and the absence of special chemical requirements and waste streams. The high quality of the glycerol by-product obtained is also a very important economic parameter. A heterogeneous catalyzed continuous process allows all these objectives to be reached.

References

[1] E.K. Wilson, Chem. Eng. News (May) (2002) 27.
[2] Biodiesel—A Success Story, Report of the International Energy Agency, February 2002.
[3] G. Vermeersch, Oléagineux. Corps Gras. Lipides, vol. 8, 2001, p. 33.
[4] X. Montagne, in: Proceedings of the Second European Motor Biofuels Forum, Graz, September, 1996.
[5] G. Hillion, X. Montagne, P. Marchand, Oléagineux. Corps Gras. Lipides, vol. 6, 1999, p. 435.
[6] U. Kreutzer, J. Am. Oil. Chem. Soc. 61 (1984) 343.
[7] R. Stern, G. Hillion, J.J. Rouxel, S. Leporq, US Patent 5,908,946 (1999).
[8] R. Stern, G. Hillion, J.J. Rouxel, US Patent 6,147,196 (2000).
[9] R.F. Vogel, R.J. Rennard, J.A. Tabacek, US patent 4,490,479 (1984).
[10] G. Gelbard, O. Brès, F. Vielfaure-Joly, J. Am. Oil. Chem. Soc. 72 (1995) 1.