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BIODIESEL PRODUCTION BY A CONTINUOUS PROCESS USING A HETEROGENEOUS CATALYST

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ABSTRACT

The production and use of biodiesel has seen a quantum jump in the recent past due to benefits associated with its ability to mitigate Green House Gas (GHG). There are large number of commercial plants producing biodiesel by trans-esterification of vegetable oils and fats based on base catalyzed (caustic) homogeneous trans-esterification of oils. However, homogeneous process needs steps of glycerol separation, washings, very stringent and extremely low limits of Na, K, glycerides and moisture limits in biodiesel. Several commercial processes to produce fatty acid methyl esters from vegetable oils have been developed and are available today. These processes consume basic catalysts such as caustic soda or sodium methylate which form unrecyclable waste products. This work provides a general description of a new process using a heterogeneous catalytic system for biodiesel production.

Key words: Biodiesel, Trans-esterification, Heterogeneous catalyst.

INRODUCTION

The production of biodiesel is greatly increasing due to its environmental benefits. However, production costs are still rather high, compared to petroleum-based diesel fuel[1]. The introduction of a solid heterogeneous catalyst in biodiesel production could reduce its price, becoming competitive with diesel also from a financial point of view. Ecological, political and economic concerns over petro diesel, which is the single largest industry in terms of dollar value on earth, are the drivers behind biodiesel production from edible/ non-edible oils and fats. Although the growth rate of plantations for vegetable oil is expanding, much of it is due to oil palm at 5% per year. The reactions for direct transformation of vegetable oils into methyl esters and glycerol have been known for more than a century[1,2].

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[3]. With over ten years of development and commercial use in Europe, biodiesel has now proved its value as a fuel for diesel engines. The product is free of sulfur and aromatics and as it is obtained from renewable sources, it reduces the life cycle of carbon dioxide emissions by almost 70% compared to conventional diesel fuel[4]. Moreover, recent European regulations have restricted sulfur content in diesel fuel to not more than 50 ppm in year 2005. Sulfur is known to provide diesel fuels with a lubricity that will

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disappear as the regulations take effect. Biodiesel addition at levels of one to two per cent in diesel blends has the beneficial impact of restoring lubricity through an anti wear action on engine injection systems[2].

EXPERIMENTAL

Biodiesel production processes

The trans-esterification of triglycerides to methyl esters with methanol is a balanced and catalyzed reaction as illustrated in Fig. 1[5]. An excess of methanol is required to obtain a high degree of conversion. Rapeseed and soybean oils are the main vegetable oil candidates for biodiesel uses. Their compositions are summarized in Table 1.

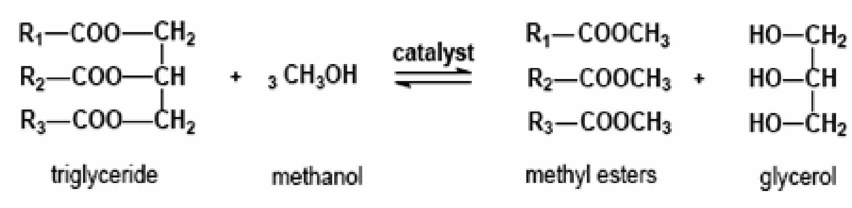

Fig. 1: Reaction for vegetable oil methanolysis

(With R_1, R_2, R_3 = Hydrocarbon chain from 15 to 21 carbon atoms)

The conventional catalysts in natural oil trans-esterification processes are selected among bases such as alkaline or alkaline earth hydroxides or alkoxides. However, trans-esterification 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[6].

Table 1: Fatty acid compositions for Rapeseed oil and Soya oil (weight %)

Fatty acid chain		Rapessed oil	Soyabean oil
Palmitic	C16 : 0	5	10
Palmitoleic	C16 : 1	< 0.5	
Stearic	C18 : 0	2	4
Oleic	C18 : 1	59	23
Linoleic	C18 : 2	21	53
Linolenic	C18 : 3	9	8
Arachidic	C20 : 0	< 0.5	< 0.5
Gadoleic	C20 : 1	1	< 0.5
Behenic	C22 : 0	< 0.5	< 0.5
Erucic	C22 : 1	< 1	

Heterogeneous catalyzed process

To avoid catalyst removal operations and soap formation, much effort has been expended on the search for solid acid or basic catalysts that could be used in a heterogeneous catalyzed process. 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[3,7]. In this paper a new continuous process is described, where the trans-esterfication reaction is promoted by a completely heterogeneous catalyst. This catalyst consists of a mixed oxide of zinc and aluminium, which promotes the trans-esterification reaction without catalyst loss. The reaction is performed at a higher temperature 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 is reached with two successive stages of reaction and glycerol separation to displace the equilibrium reaction[5]. The flow sheet for this process is shown in Fig. 2.

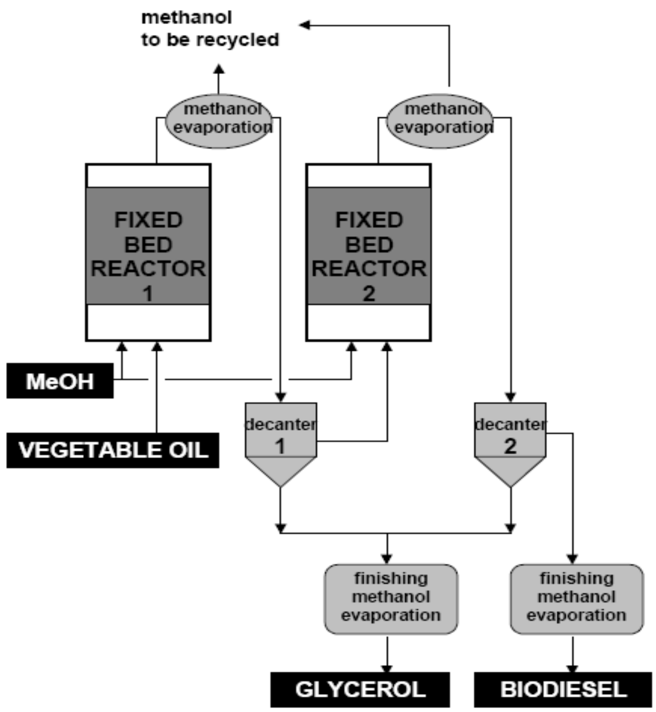

Fig. 2: Scheme for a continuous heterogeneous catalyzed process

The catalyst section includes two fixed bed reactors, that are fed by oil and methanol at a given ratio. Excess methanol is removed after each of the two reactors by a partial flash. Esters and glycerol are then separated in a settler[6]. Glycerol phases are joined and the last traces of methanol are removed by vaporization. Biodiesel is recovered after final recovery of methanol by vaporization under vacuum and then purified to remove the last traces of glycerol[7]. Typical characteristics of biodiesel obtained from rapeseed oil and soybean oil in pilot plant operations are reported in Table 2.

Table 2: Main characteristics of the biodiesel fuels obtained from Rapesee oil and Soybean oil with heterogeneous catalyzed process

Characteristics of biodiesel		From rapeseed oil	From soyabean oil	Required european specifications
Methyl esters	Wt- %	> 99.0	> 99.0	96.5
Monoglycerids	Wt- %	0.5	0.5	0.8
Diglycerides	Wt- %	0.02	0.02	0.2

Cont…

Characteristics of biodiesel		**From rapeseed oil**	**From soyabean oil**	**Required european specifications**
Triglycerides	Wt- %	0.01	0.01	0.2
Free glycerol	Wt- %	< 0.02	< 0.02	0.2
Total glycerol	Wt- %	0.15	0.15	0.25
Acid number	mg KOH/Kg	< 0.3	< 0.3	0.5 max
Water content	mg/Kg	200	200	500 max
Metal content	mg/Kg	< 3	< 3	-
Phosphorus	mg/Kg	< 10	< 10	<10

General conditions: methanol/vegetable oil ratio : 1; Temperature : 200°C ; LHSV : 0.5 h^{-1}

Table 3: Compositions of ester phases obtained from two sucessive fixed bed reactor (Weight %) neutralized or acidic oil

Feedstock composition			**Reactor 1**		**Reactor 2**	
Rapeseed oil (wt %)	**Oleic acid (wt %)**	**Acid index**	**Methyl esters (wt %)**	**Acid index**	**Methyl esters (wt %)**	**Acid index**
100	0	< 1	94.5	0.15	99.0	0.15
95	5	11	86.8	2.1	98.3	0.4

General condition: methanol/vegetable oil ratio: 1; Temperature: 200°C; LHSV: 0.5 h^{-1}

CONCLUSION

Nowadays, biodiesel is produced in great amount and its production continues to grow. 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 attained.

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