

Raw material for biodiesel production. Valorization of used edible oil

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Résumé - La production des biocarburants est un domaine d'actualité pour les chercheurs en raison de la pertinence qu'elle gagne tous les jours, et c'est en raison de la hausse du prix du pétrole et les avantages environnementaux. Le biodiesel est une voie prometteuse pour réduire la dégradation environnementale par l'augmentation des polluants, y compris les émissions de gaz à effet de serre (CO₂ d'origine fossile, les oxydes d'azote et de soufre). Le prix de biodiesel est en rapport direct avec le coût des matières premières, (70-95 % du coût total de biodiesel). Dans ce contexte, le but de cet article est d'étudier les différentes ressources renouvelables qui peuvent être utilisées comme matière première pour la production de biodiesel en mettant l'accent sur la possibilité de l'utilisation des huiles comestibles usagées. L'attention particulière est accordée à l'optimisation de la production de biodiesel, à partir d'huile comestible usagée par la réaction de trans estérification.

Abstract – Biofuel's production is a topical domain for researchers due to the relevance that it is winning every day. This, because of the increase in the petroleum price and the environmental advantages. Biodiesel is a promising way to reduce the environmental degradation by increasing pollutants including greenhouse gas emissions (fossil CO₂, nitrogen and sulfur oxides). Biodiesel price is directly related to the cost of the used raw materials (70-95 % of the total biodiesel cost). In this context, the purpose of this paper is to study the different renewable resources which can be used as raw material for biodiesel production to emphasize the possibility of the use of edible used oils. The special attention is paid to optimization of biodiesel production from used edible oil by trans esterification reaction.

Key words: Renewable energy - Biodiesel feed stocks - Waste cooking oil.

1. INTRODUCTION

During the past decades worldwide petroleum consumption has permanently increased due to the growth of human population and industrialization, which has caused depleting fossil fuel reserves and increasing petroleum price. On the other hand, combustion of fossil fuels contributes most to emissions of greenhouse gases (GHG), which lead to atmospheric pollution and global warming [1].

Renewable energy can be considered as alternatives to fossils energies. They are already used in many countries around the world. Globally, 15 % of primary energy supply comes from renewable sources [2]. Biomass is the most common form of renewable energy and is, among the renewable forms of energy, the major source of the

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primary energy supply [3]. Renewable resources accounts for about 10 % of the world's energy consumption and can be converted to other usable forms of energy like biofuels [4]. Among biofuels, biodiesel is one of the possible alternatives in the transport section [5].

Biodiesel is a non-toxic, biodegradable, renewable fuel that can be produced from a range of organic and renewable raw material including fresh or waste vegetable oils, animal fats, and oilseed plants. Biodiesel has significantly lower emissions than petroleum-based diesel when it is burned, whether used in its pure form or blended with petroleum diesel. It does not contribute to a net rise in the level of carbon dioxide in the atmosphere and leads to minimize the intensity of greenhouse effect [6, 7]. In addition, biodiesel is better than diesel fuel in terms of sulphur content, flash point, aromatic content and biodegradability [8].

Developing countries have a comparative advantage for biodiesel production because of greater availability of land, favourable climatic conditions for agriculture and lower labor costs [9]. In developed countries there is a growing trend towards employing modern technologies and efficient bioenergy conversion using a range of biofuels, which are becoming cost-wise competitive with fossil fuels [10]. Many studies have investigated the environmental benefits and impacts of biodiesel [11, 12].

The successful introduction and commercialization of biodiesel in many countries around the world has been accompanied by the development of standards to ensure high product quality and user confidence. Some biodiesel standards are ASTM D6751 (American Society for Testing and Materials) and EN 14214 (European norm) [13].

Biodiesel fuel is recently attractive increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines [14]. For example, B5 used in Europe contains 5 % of biodiesel (B100) and 95 % of petro diesel. Biodiesel blends up to B20 can be used in nearly all diesel equipment and are compatible with most storage and distribution equipment. These low-level blends generally do not require any engine modifications [15].

There are different potential raw materials for biodiesel production. Currently, edible oils are the main resources for world biodiesel production. However, there are many reasons for not using it. In this context, the main of this paper is to study the different renewable resources which can be used as raw material for biodiesel production and to present the possibilities of the use of edible used oils into this production. The special attention is paid to the optimization of biodiesel production from waste edible oil by transesterification reaction.

2. RAW MATERIAL FOR BIODIESEL PRODUCTION

2.1 Edible plant oils

Biodiesel has been predominantly (more than 95 %) produced from edible vegetable oils (biodiesel first generation) all over the world, which are easily available on large scale from the agricultural industry [16]. Currently, biodiesel is mainly prepared from rapeseed in Canada, soybean in US, sunflower in Europe and palm in Southeast Asia [17]. However, continuous and large scale production of biodiesel from edible oils has recently been of great concern because they compete with food materials [18]. Knowing that, nearly 60 % of humans in the world are malnourished [19].

The largest biodiesel producers were the European Union, the United States, Brazil, Indonesia, with a combined use of edible oil for biodiesel production of about 8.6 million tons (7.8 million hectares were used) in 2007 [20]. The estimated increase in edible oil use for biodiesel production was 6.6 million tons from 2004 to 2007, which would attribute 34 % of the increase in global consumption to biodiesel [20].

Between 2005 and 2017, biodiesel use of edible oils is projected to account for more than a third of the expected growth in edible oil use [21], which means rise of biomass price, increase in water requirement and problem in water availability, and particularly, more land somewhere in the world will be converted into farmland, thereby releasing GHG emissions. Because of these disadvantages, researchers have sought other renewable resources for biodiesel production.

2.2 Non-edible plant oils

Technologies are being developed to exploit cellulosic materials for the production of biodiesel (biodiesel, second generation) such as leaves and stems of plants, biomass derived from waste, and also, oils seeds from non-edible plants.

Non-edible biodiesel crops are expected to use lands that are largely unproductive and those that are located in poverty stricken are a sand in degraded forests. Moreover, non-edible oil plants are well adapted to arid, semi-arid conditions and require low fertility and moisture demand to grow. Added to this, non-edible oils are not suitable for human food due to the presence of toxic components in the oils [22]. For all these reasons, the use of non-edible oils as raw material is a promising way in biodiesel production.

There are a large number of oil plants that produce non-edible oils. From a list of 75 plant species containing oil in their seeds or kernels, 26 species were reported by Azam *et al.*, [23] as potential sources for biodiesel production. The important non edible oil plants are jatropha, karanja, tobacco, mahua, neem, rubber, sea mango, castor, cotton [23]. Of these feedstocks, jatropha, moringa and castor oils are the most often used in biodiesel production.

In Algeria, Castor oil is findable but it is not very current. Added to this, the biodiesel produced from castor oil present a very elevated value of viscosity compared to the value imposed by the American norm (ASTM D6751) and the European norm (EN14214). Moringa was planted in Mascara (359 km West of Algiers), where the climate of the region was not really suitable for its development. Also, moringa comes just barely be planted in Tamenrasset (1970 km South of Algiers) and in the 'Institut Technique de l'Arboriculture Fruitière ITAF' (Algiers) but its potential of development is not yet put in evidence. Jatropha has been planted in Adrar (1543 km South of Algiers) as part the JatroMed project which has as purpose the cultivation of jatropha to check its potential development in Algeria. JatroMed involves five countries from the Mediterranean region: Greece (project coordinator), Italy, Egypt, Morocco and Algeria.

The non-edible oils plant are called to solve the problem of competition with food production. However, the problem of water requirement, water availability, and mainly, the quantity of GHG generated by the great rate of exploitable land could not be solved using this raw material.

2.3 Used edible oils

There are several end-uses for used edible oil (commonly called Waste Cooking Oil, 'WCO'), such as the production of soaps or of energy by anaerobic digestion or thermal cracking. However, because of the poor quality of soap produced from WCO, a large

amounts of WCO are illegally dumped into rivers and landfills, causing environmental pollution. Hence the management of such oils and fats pose a significant challenge because of their disposal problems and possible contamination of the water and land resources.

The production of biodiesel from WCO to partially substitute petroleum diesel is one of the measures for solving the twin problems of environment pollution and energy shortage [24]. Also, in order to reduce the cost of biodiesel production, WCO would be a good choice as raw material since it is cheaper than virgin vegetable oils and other feedstocks [25].

The used edible oil is categorized by its Free Fatty Acid (FFA) content. If the FFA content of WCO is $< 15\%$, then it is called 'yellow grease'; otherwise, it is called 'brown grease' [26]. The amount of WCO generated in each country is huge and varies depending on the use of vegetable oil.

2.4 Microalgae

Microalgae as a raw material for biodiesel (biodiesel third generation) has been reviewed extensively in recent years [26, 27]. They are photosynthetic microorganisms that convert sunlight, water and CO_2 to algal biomass. Microalgae are classified as diatoms (bacillariophyceae), green algae (chlorophyceae), golden brown (chrysophyceae) and blue green algae (cyanophyceae) [27].

The microalgae have long been recognized as potentially good sources for biofuel production because of their high oil content (more than 20%) and rapid biomass production. Algae biomass can play an important role in solving the problem between the production of food and that of biofuels in the near future. The cultivation of microalgae does not need much land as compared to that of terraneous plants.

Due to their high viscosity (about 10–20 times higher than diesel fuel) and low volatility, microalgae do not burn completely and form deposits in the fuel injector of diesel engines [14]. The transesterification of microalgal oils will greatly reduce the original viscosity and increase the fluidity.

2.5 Animal fats

Animal fats used to produce biodiesel include tallow [28], choice white grease or lard [29], fish fat (in Japan) and chicken fat. Compared to plant crops, these fats frequently offer an economic advantage because they are often priced favorably for conversion into biodiesel.

Animal fat methyl ester has some advantages such as high cetane number, non-corrosive, clean and renewable properties. Animal fats tend to be low in FFAs and water, but there is a limited amount of these oils available, meaning these would never be able to meet the fuel needs of the world.

3. EXPERIMENTAL

3.1 Transesterification reaction

Physicochemical properties are the main the use of direct WCO in conventional diesel engines. The transesterification reactions the most common method of converting triglycerides (TAG) from oils into methyl esters (biodiesel). The conversion of WCO into biodiesel through the transesterification process reduces the molecular weight to

one-third, reduces the viscosity by about one-seventh, reduces the flash point slightly, increases the volatility marginally and reduces pour point considerably [27]. Then, the fuel produced has approximately the same property of petrodiesel and can be used in conventional diesel engines without any change in this last.

The main factors affecting transesterification reaction and produced esters yield are: the molar ratio of alcohol: oil, type of alcohol, type and amount of catalyst, reaction temperature, pressure and time, mixing intensity as well as the contents of Free Fatty Acids (FFA) and water in oils. The reaction is produced as shown in the figure 1.

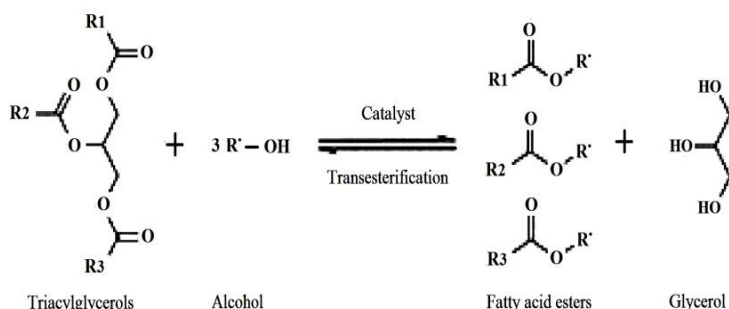


Fig. 1: Transesterification reaction of triglycerides with alcohol

3.2 Protocol adopted

The used oil is first pretreated before being transesterified. Preprocessing consists in oil filtration to eliminate any suspended material and heating to 100 ° to evaporate the water contained. After establishment of pretreatment, a volume of alcohol was added to a mass of used sunflower oil. The reaction for the production of biodiesel was carried out with a 6:1 fixed ratio of alcohol: sunflower oil, with 1% catalyst (NaOH), under constant mixing and controlled temperature.

Thus, the cleavage of triacyl glyceride molecules occurred, producing a mixture of the methyl esters of corresponding fatty acids and glycerin as a co-product. The yield (Yd) of the transesterification reaction is calculated using (1), where Experimental mass designates the oil extracted mass and Theoretical mass designates the initial oil mass.

$$\text{Yd (\%)} = \text{Experimental mass} / \text{Theoretical mass} \times 100 \quad (1)$$

The protocol is adopted using ethanol and methanol as alcohol at 40° in order to determine the alcohol that give the best yield. A series of experiments with reaction times ranging from 25 to 175 minutes (mn) were performed to fix the best reaction time.

4. RESULTS AND DISCUSSION

4.1 Type of alcohol

Yields of the transesterification of used sunflower oil following the protocol adopted, according to reaction time and using methanol and ethanol as alcohol are grouped in figure 2.

Results clearly show that the methanol gave a higher yield compared to the ethanol, and this whatever the reaction time. The production of biodiesel using ethanol is more

complicated than that using methanol. This is explained by the fact that the use of ethanol leads to the formation of a stable emulsion.

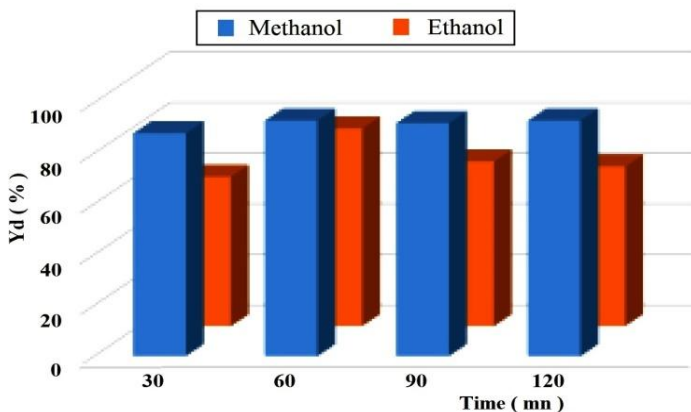


Fig. 2: Effect of alcohol type on the yield of sunflower oil transesterification

In the case of methanol, emulsions are easily decomposed to form an upper layer rich in methyl esters and a lower layer rich in glycerol. In the case of ethanol, emulsions are more stable and complicate the separation of the two layers. That, because of the physical structure of ethanol which has a larger non-polar group than that of methanol.

In literature, we also found that the most commonly used alcohols are ethanol and methanol, especially the latter seen its low cost and its physical benefits (chains shorter and more polar alcohol). However, ethanol has the advantage to come from a renewable source by fermentation of sugar derived from sugar cane or beet. Biodiesel thus obtained is 100 % renewable.

4.2 Reaction time

The yields of the sunflower oil transesterification following the protocol adopted and according to reaction time are grouped in figure 3.

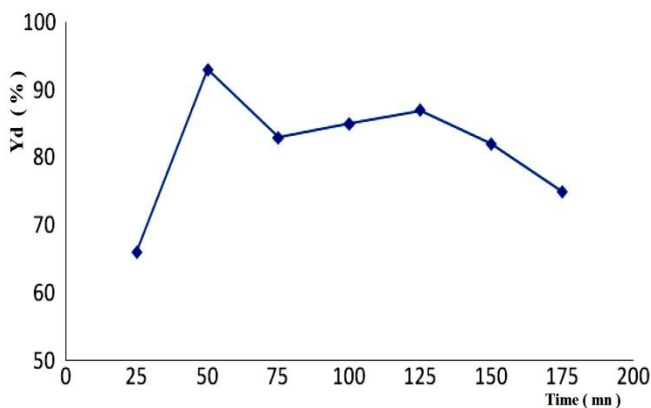


Fig. 3: Effect of reaction time on the yield of sunflower oil transesterification

Results clearly show that the transesterification reaction at 50 min gave a higher yield compared to the reaction at others times.

The reaction at 40° takes place in two phases: a rising phase with a peak at 50 min (yield = 93 %) representing the optimum of the transesterification reaction and a continuously decreasing phase from 50 min to 120 min.

The results can be explained by the fact that reaction time lower than 50 minutes is not enough for methanol to transesterify all the triacylglycerols contained in oil. However, reaction time above than 50 minutes favors the triggering of a hydrolysis reaction of esters due to the water formed during the dissolution of sodium hydroxide in methanol.

5. CONCLUSION AND OUTLOOK

Biodiesel resolve environmental pollution by fuel combustion emission and increase of the world energy demand problem. WCO is a waste causing environmental problems if directly discharged in the receptor receiver. Then, the use of WCO as raw material in biodiesel production is a potential solutions to these troubles.

Legislation that would make collect of WCO possible in Algeria remains absent. Hence, it is currently impossible to produce biodiesel from WCO on an industrial scale unlike many countries in the world (Spanish, Germany and French). Then, the problems caused by this waste are not solved. This why, establishing legislation and creating laws to officially collect this waste in order to valorise it in renewable energy production is a smart idea.

Of several possible methods for biodiesel production from WCO, their transesterification reaction with an alcohol in the presence of a catalyst is the most suitable method. The experimental results show that the methanol gave a higher yield compared to the ethanol, and this whatever the reaction time. Results show also that 50 minutes is the optimum time for the transesterification reaction of triacylglycerols carried out to produce biodiesel from used sunflower oil at 40 °C and using sodium hydroxide as catalyst.

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