Potential Alternatives to Vegetable Oils for Biodiesel Production. Sunflower oil application

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***Abstract*— The rising demand for fuel together with deteriorating climate conditions has raised concerns for energy crisis and environmental problems. Biofuels are a promising way to reduce the environmental degradation by increasing pollutants including greenhouse gas emissions. Most current research on renewable fuel is considerably focused on producing biodiesel from vegetable oils. The aims of this paper are to highlight the possibilities of the use of vegetable oils for biodiesel production and to establish an inventory of oil seeds plant species having a high oil content dedicated to biodiesel production crops. In experimental, effect of reaction time on the yield of the sunflower oil transesterification has been studied.**

***Keywords*— Renewable Energy, Biodiesel, Vegetable Oils, Sunflower Oil, Transesterification.**

INTRODUCTION

The finite nature of fossil fuels, increasing concerns regarding environmental impact, especially related to greenhouse gas emissions, the dramatic increase in the price of petroleum, and health and safety considerations are forcing the search for new energy sources [1,2]. Renewable energies are considered important resources in many countries around the world. However, on a global scale, less than 15% of the primary energy supply comes from renewable sources [3]. Biomass is the most common form of renewable energy and is, among the renewable forms of energy, the major source of the primary energy supply [4]. It accounts for about 10% of the world's energy consumption and can be converted to other usable forms of energy like biofuels [5].

Among biofuels, biodiesel is one of the possible alternatives to petroleum [6]. Biodiesel is generally classified as fatty acid esters, derived from the catalyzed transesterification of fats and oils generally with methanol [7]. The general conclusion from the literature is that, in terms of power, wear, efficiency and emissions, biodiesel is a viable alternative [8]. Developing countries have a comparative advantage for biodiesel production because of greater availability of land, favorable 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]. In recent years, many studies have investigated the environmental impacts of the biodiesel [11], [12].

Most current research on biorenewable fuel is considerably focused on producing biodiesel from vegetable oils [13], [14]. This production has been debated recently because the use of fertile lands needed to produce biofuels increase prices of staple foods and making them more scarce which is dangerous to the food security of poor people around the world [15]. This why it is smarter to produce biodiesel from vegetable species not intended for food.

In this context, the main objective of our work is the establishment of an inventory of oil seeds plant species having a high oil content dedicated to biodiesel production crops. As application, effect of reaction time on the yield of sunflower oil transesterification is studied.

I. RESOURCES FOR BIODIESEL PRODUCTION

Resources for biodiesel production can be traditionally categorised into three main groups [16], vegetable oils (edible and non edible), animal fats and waste cooking oils (used oily materials). Additionally, algal oils have been emerging in recent years as the fourth category of growing interest because of their high oil content and rapid biomass production [17]. Different kinds of vegetable edible oils, depending upon the climate and soil conditions, are being used as the main conventionally feedstocks for biodiesel production such as rapeseed oil in Canada, sunflower oil in Europe, palm oil in Southeast Asia, etc. However, the higher prices of edible oils than that of fossil fuels, the lower cost of non edible oil plant cultivation, the rapidly growing world population and extensive human consumption of edible oils (large demand for edible oils as food) cause some significant problems, for instance, starvation in developing countries. Therefore, non edible plant oils become very promising alternative feedstocks for biodiesel production [18].

II. MOST USED NON EDIBLE OILS

Various oils extracted from seeds or kernels of non edible crops are potential feedstocks for biodiesel production. The important non edible oil plants are jatropha [19], karanja [19], tobacco [20], mahua [21], neem [22], rubber [23], sea mango [24], castor [25], cotton [26]. Of all these feedstocks, jatropha, karanja, mahua and castor oils are the most often used in biodiesel synthesis. Table 1 [27] presents a summary on the oily plants and the oil contents of their seeds or kernels based on a wide literature survey.

TABLE I
OIL CONTENT IN SEEDS AND KERNELS OF SOME NON-EDIBLE PLANTS

Name	Oil Seed Content %	Oil Karnel Content %
Jatropha Curcas	20–60	40–60
Pongamia Pinnata	25–50	30–50
Azadirachta indica	20–30	25–45
Madhuca indica	35-50	50
Schleichera triguga	10.65	
Ricinus communis	45–50	
Linumusita tissimum	35–45	
Cerbera odollam (Cerberamanghas)	54	6.4
Gossy piumsp	17–25	17
Nicotiana tabaccum	36–41	40–50
Argemone mexicana	22–36	
Hevea brasiliensis	40–60	
Melia azedarach	10	
Simmondsia chinensis	45–55	67
Thevetia peruviana	8.41	
Moringa oleifera	33–41	2.9
Thlaspiarvense	20–36	
Euphorbia lathyris	48	
Sapium sebiferum	12–29	
Pistacia chinensis	30	
Daturastramonium	10.3–23.2	

III. ADVANTAGES AND DISADVANTAGES OF NON EDIBLE OILS

Advantages of non edible oils Preliminary evaluation of several non edible oil seed crops for their growth, feedstock and adaptability show that these feedstocks have the following advantages [28]:

- The adaptability of cultivating non edible oil feedstocks in marginal land and non agricultural areas with low fertility and moisture demand.
- They can be grown in arid zones (20cmrainfall) as well as in higher rainfall zones and even on land with theirs oil cover. Moreover, they can be propagated through seed or cuttings.
- They have huge potential to restore degraded lands, create rural employment generation and fixing of up to 10t/ha/yr CO2 emissions.
- They do not compete with existing agricultural resources.
- They eliminate competition for food and feed. Non edible oils are not suitable for human food due to the presence of some toxic components in the oils.
- Conversion of non edible oil into biodiesel is comparable to conversion of edible oils in terms of production and quality.
- Less farmland is required and a mixture of crops can be used. Non edible oil crops can be grown in poor and waste lands that are not suitable for food crops.
- Non edible feedstock can produce useful by products during the conversion process, which can be used in other chemical processes or burned for heat and power generation. For instance, the seed cakes after oil expelling can be used as fertilizers for soil enrichment.
- Most of non edible oils are highly pest and disease resistant.
- The main advantages of non edible oil are their liquid nature portability, ready availability, renewability, higher heat content, lower sulfur content, lower aromatic content and biodegradability.

However, biodiesel produced from non edible oils present numerous disadvantages because of it's:

- High viscosity.
- Low volatility.
- High percentage of carbon residue.
- Reactivity of unsaturated hydrocarbon chains.

IV. CULTURE OF NON EDIBLE OILS

Only several, most important and most frequently used non edible oils were selected for further discussion.

A. *In the world*

Jatropha plant is one of the most promising potential oil sources for biodiesel production in South-East Asia, Central and South America, India and Africa. Today, it is the major feedstock for production of biodiesel in developing countries like India, where the annual production is about 15,000 t [29]. It can grow almost anywhere, on waste, sandy and saline soils, under different climatic conditions as well as under low or high rainfall and frost. Its cultivation is easy, without intensive care and minimal effort. Its healthy life cycle of 30–50 years eliminates the yearly replantation. Jatropha oil content varies depending on the types of species, but it is about40–60% in the seeds and 46–58% in the kernels. Jatropha has comparable properties to diesel, such as calorific value and cetane number. It has a great potential as an alternative fuel since it does not require any modification of the engine [29]. The serious problem with jatropha oil is its toxicity to people and animals.

Karanja is a nitrogen-fixing tree producing seeds with significant oil content. It is a leguminous, medium size hardy tree with fast growing, which is native to India, the United States, Indonesia, Australia, Philippines and Malaysia. Karanja oil has many toxic substances that do not allow its use as cooking oil. Annual production of karanja oil in India is 55,000 t [29], of which only 6% is currently used. It can be cultivated to improve the soil quality, and the exhausted land can be reused for the agricultural purpose.

Castor plant is easily grown as a weed and has similar ecological requirements as jatropha. It is native to India, China, Brazil, some countries of ex-USSR and Thailand. Castor oil is completely soluble in alcohols and has a viscosity up to 7-times higher than that of other vegetable oils. The high viscosity of crude castor oil is a problem for its direct use as a fuel.

Mahua and neem trees, medium to large trees found in most parts of India and Burma, are a significant source of oils. Almost the whole tree of neem is usable for various purposes in the medicine and as pesticides and organic fertilizer [29]. Kernels of mahua contain up to 50% of oil, which contains about 20% FFAs making the procedure for biodiesel production from this oil very required [21].

The major regions of kusum tree production are located in India, Sri Lanka, Timor and Java. Bitter in taste and toxic, kusum oil has about 5–11% FFA. The pure oil cannot be used as a fuel because of its high viscosity [29].

Sea mango tree, well-known as a “suicide tree”, grows in India, Madagascar, Malaysia, Sri Lanka and Cambodia. Having a high oil content (54%), its seeds are a worth source for biodiesel production, which has been used so far only in a transesterification process with a specific solid catalyst.

Greece and Turkey are two the main producers of cotton in the European Union and world. Cottonseeds are a source of one of the cheapest vegetable oil having extreme viscosity and high density. Refined cottonseed oil production in Turkey in 1997 was 20,546 t.

However, crop production is inconsistent according to harvest area and climatic conditions. Several non edible oils have been isolated from various plants all over the world such as Moringa oleifera, Argemone mexicana, Euphorbia lathyris or Pistacia chinensisbge [27].

Beside many medicinal uses and significant nutritional value, M. oleifera oil has great potential for biodiesel production. After extraction of vitamin A and other high valuable constituents, the oil can be converted to biodiesel without any waste [27].

T. arvense, known as field pennycress or stinkweed, is native to North America and Eurasia. It is highly adapted to a wide variety of climatic conditions, tolerant of fallow lands and requires minimal agricultural inputs (fertilizer, pesticides, water).

Meals from defatted seeds cannot be used as an animal feed because of high contentof glucosinolate. Because of high oil content (20–36%), the field pennycress seeds are an acceptable feedstock for biodiesel production [27].

E. lathyris and S. sebiferum produce also significant amounts of oil in their seeds. Primarily, the both plants are native to China and adapted to alkaline, saline, droughty and acidic soils [27].

B. In Algeria

Castor oil is findable in Algeria, 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). This why, it is not really interesting for us.

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). The potential of development is not yet put in evidence.

Jatropha also has been planted in small amount (to check its potential development) in Adrar (1543 Km south of Algiers): The JatroMed project is focusing on the cultivation of this plant and it involves five countries from the Mediterranean region: Greece (project coordinator), Italy, Egypt, Morocco and Algeria.

V. EXPERIMENTAL

Because of the non ready availability of non edible crops with great potential oil for biodiesel production in Algeria, we are interested to the biodiesel production from edible oil. We chose the used sunflower oil with a view to eliminate it as waste on the one hand, and produce biorenewable fuel on the other hand.

A. Chemical production of biodiesel

Viscosity is the main barrier that prevents the use of direct vegetable oils in conventional diesel engines. Therefore, there are many techniques, methods and processes that have been used recently to produce biodiesel from oily plant species (edible and non edible). These methods include pyrolysis, micro emulsification, dilution, and transesterification.

This last is the most common method of converting Triglycerides (TAG) from oils into biodiesel and the most promising solution of the high viscosity oil problem. 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 transesterification reaction can be non-catalyzed or catalyzed by an acid, a base or an enzyme. Depending on the solubility of the chemical catalyst in the reaction mixture, transestérification reaction can be homogeneously or heterogeneously catalyzed. These reactions can be accomplished as one-step (base or acid) or two-step (acid/base) processes, depending on the content of FFA, as shown in Fig. 1.

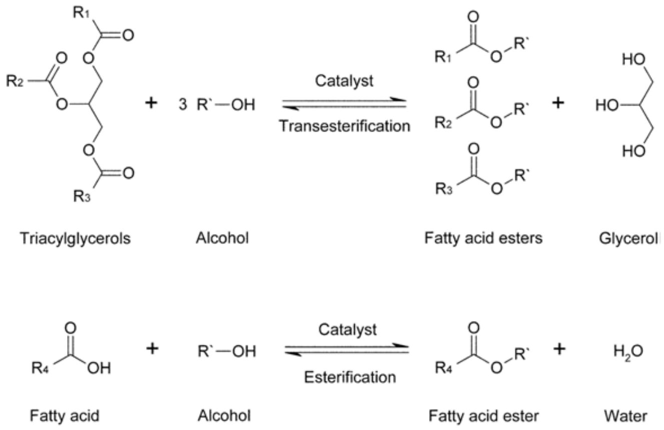

Fig. 1 Transesterification and esterification reactions carried out during biodiesel production from triacylglycerols or free fatty acids

B. Experimental Protocol adopted

To produce biodiesel by transesterification, we are obliged to study the various factors affecting the reaction mentioned above. In this work, we study the time effect of the transesterification reaction.

Among alcohols that can be used in the transesterification process, we find methanol, ethanol, propanol, butanol and amyl alcohol. The work of Meher [30] show that the methanol gave a higher yield, this why we have chosen it in our work.

A volume of alcohol was added to a mass of used sunflower oil (after establishing a pretreatment). The reaction of biodiesel production was carried out with a 6:1 fixed ratio of methanol: sunflower oil with 1% catalyst (sodium hydroxide NaOH), under constant mixing and controlled temperature (40°C). Thus, the cleavage of triacylglycerols molecules occurred, producing a mixture of the methyl esters of corresponding fatty acids and glycerin as a co-product.

A series of experiments with reaction times ranging from 25 to 175 minutes (mn), were performed.

The yield (*Yd*) of the transesterification reaction is calculated using (1).

$$Yd\% = \frac{Experimentalmass}{Theoreticalmass}.100, \quad (1)$$

Experimental mass designates the oil extracted mass (reaction product) and Theoretical mass designates the initial oil mass.

C. Results and discussion

The yields of the sunflower oil transesterification following the protocol adopted and according to reaction time are grouped in Fig. 2.

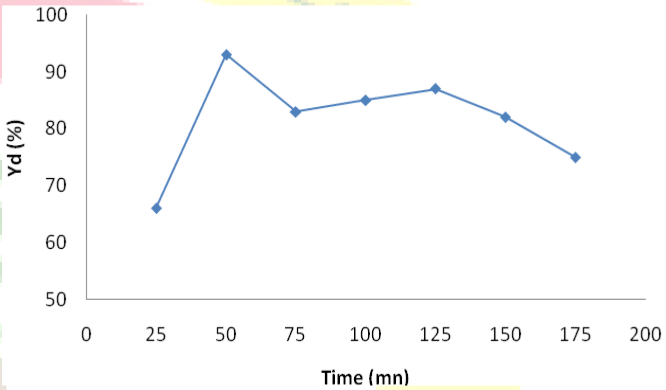

Fig. 2 Yields of sunflower oil transesterification according to reaction time

Results clearly show that the transesterification reaction at 50 mn 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.
- A continuously decreasing phase from 50 mn to 120 mn.

The results can be explained by the fact that reaction time lower than 50 minutes is not enough for methanol to transesterifiy 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, as shown in Fig. 3.

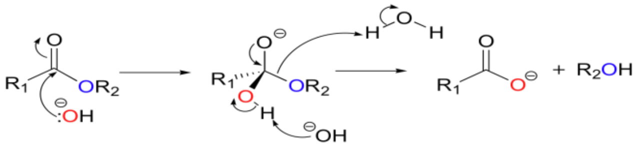

Fig. 3 Hydrolysis reaction of esters in due to the water formed during the dissolution of sodium hydroxide in methanol

The consummation of esters during hydrolyses reaction is the principal factor induces a decrease in yields.

VI. CONCLUSIONS

Because of environmental pollution by fuel combustion emission and an increase of the world energy demand, the vegetable oils have become the leading raw materials for obtaining biodiesel. Of several possible methods for biodiesel production from vegetable oils, their transesterification reaction with an alcohol in the presence of a catalyst is the most suitable method. The experimental results show that 50 minutes is the optimum time (a higher yield is detected) 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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