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# Biodiesel: Spent wash and By-Products

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**Abstract—**An ever increasing demand of fuels has been a challenge for today's scientific workers. The fossil fuel resources are dwindling day by day. Biodiesel seems to be a solution for future. Biodiesel is an environmentally viable fuel. Out of the four ways viz. direct use and blending, micro-emulsions, thermal cracking and transesterification, most commonly used method is transesterification of vegetable oils, fats, waste oils, etc. The purpose of the transesterification process is to lower the viscosity of the oil. Biodiesel fuel is a renewable substitute fuel for petroleum diesel or petro diesel fuel made from vegetable or animal fats; it can be used in any mixture with petro diesel fuel, as it has very similar characteristics, but it has lower exhaust emissions. it is renewable, biodegradable, non-toxic, and essentially free of sulfur and aromatics. Biodiesel seems to be a realistic fuel for future; it has become more attractive recently because of its environmental benefits. Biodiesel wash water which contains chemicals like alcohol, traces of Sulphuric acid, KOH/ NaOH. This effluent is called as Brine Solution. The biodiesel spent wash and by-products like glycerine has potential economic benefits which will reduce the treatment to given for such effluents coming out of biodiesel production plants.

**Keywords**—Biodiesel, Transesterification, Brine solution, Potassium, Glycerine

## I. INTRODUCTION

The scarcity of conventional fossil fuels, growing emissions of combustion-generated pollutants, and their increasing costs will make biomass sources more attractive [1]. Petroleum-based fuels are limited reserves concentrated in certain regions of the world. These sources are on the verge of reaching their peak production. The fossil fuel resources are shortening day by day. The scarcity of known petroleum reserves will make renewable energy sources more attractive [2]. Biodiesel (Greek, bio, life + diesel from Rudolf Diesel) refers to a diesel-equivalent, processed fuel derived from biological sources. Biodiesel fuels are attracting increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines. Biodiesel, as an alternative fuel for internal combustion engines, is defined as a mixture of mono alkyl esters of long chain fatty acids (FAME) derived from a renewable lipid feedstock, such as vegetable oil or animal fat. Biodiesel typically comprises alkyl fatty acid (chain length C14–C22) esters of short-chain alcohols, primarily, methanol or ethanol. Biodiesel is now mainly being produced from soybean, rapeseed, and palm oils. Glycerol (or glycerine; 1,2,3-propanetriol) is produced in addition to FAME during transesterification of vegetable oils and animal fats . Prior to the increase in biodiesel production that occurred over the past decade as a result of the continued interest in renewable fuels, the market demand for glycerol was relatively balanced with supply. However, the emergence of the biodiesel industry has generated a surplus of glycerol, which has spawned numerous efforts to find new applications, products, and markets using this versatile chemical. Several methods have been used to separate fatty acid methyl esters (FAME) from other components. However, there are two generally accepted methods to purify biodiesel: wet and dry washing. The more traditional wet washing method is widely used to remove excess contaminants and leftover production chemicals from biodiesel. Since both glycerine and methanol are highly soluble in water, water washing is very effective in removing both contaminants and until recently was the most common method of purification. It also has the advantage of removing any residual sodium salts and soaps, the latter being a by-product of high FFA feeds, due to their water solubility. However, the inclusion of additional water to the process offers many disadvantages, including increased cost and production time. A highly polluting liquid effluent is generated. Significant product loss can be carried out for retention in the water phase. Furthermore, emulsion formation when processing used cooking oils or other feeds with high FFA content can happen due to the soap formation [1]. Biodiesel effluent is waste water discharged from the biodiesel production units during the process of biodiesel production, where the biodiesel was washed with water to remove the suspended matter and catalysts present in it.

## II. POTASSIUM AS PLANT NUTRIENT

Potassium (K) is one of sixteen essential nutrients required for plant growth and reproduction. It is classified as a macronutrient, as are nitrogen (N) and phosphorus (P). The chemical symbol for potassium is "K." It is taken up by plants in its ionic form (K+).The word potassium translates from the Latin or German word, Kalium. The term "potash" comes from the colonial practice of burning wood in large pots and using the ashes as fertilizer and making soap, gunpowder and glass. "Potash" is defined as $K_2O$ and is used to express the content of various fertilizer materials containing potassium, such as muriate of potash (KCl), sulfate of potash ($K_2SO_4$), nitrate of potash ($KNO_3$). While potassium is not a constituent of any plant structures or compounds, it plays a part in many important regulatory roles in the plant. It is essential in nearly all processes needed to sustain plant growth and reproduction. Potassium plays a vital role in Photosynthesis, Translocation of photosynthates, Protein synthesis, Control of ionic balance, Regulation of plant stomata and water use, Activation of plant enzymes, It is known to activate at least sixty enzymes involved in plant growth. And, this may be its most important function in the plant. Plants deficient in potassium are less resistant to drought, excess water, and high and low temperatures. They are also less resistant to pests, diseases and nematode attacks. Potassium is also known as the quality nutrient because of its important effects on quality factors such as size, shape, colour, taste, shelf life, fibre quality and other quality measurements. Plants absorb potassium as the potassium ion (K+). Potassium is a highly mobile element in the plant and is translocated from the older to younger tissue. Consequently, potassium deficiency symptoms usually occur first on the lower leaves of the plant and progress toward the top as the severity of the deficiency increases. One of the most common signs of potassium deficiency is the yellow scorching or firing (chlorosis) along the leaf margin. In severe cases of potassium deficiency the fired margin of the leaf may fall out. However, with broadleaf crops, such as soybeans and cotton, the entire leaf may shed resulting in premature defoliation of the crop. Potassium deficient crops grow slowly and have poorly developed root systems.

## III. ALKALI CATALYTIC TRANSESTERIFICATION METHODS

In the alkali catalytic methanol transesterification method, the catalyst (KOH or NaOH) is dissolved into methanol by vigorous stirring in a small reactor. The oil is transferred into a biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil. The final mixture is stirred vigorously for 2 h at 340 K in ambient pressure. A successful transesterification reaction produces two liquid phases: ester and crude glycerol. The alkali-catalysed transesterification of vegetable oils proceeds faster than the acid-catalysed reaction. The first step is the reaction of the base with the alcohol, producing an alkoxide and a protonated catalyst. For oil samples with FFA below 2.0%, alkaline transesterification is preferred over the acid catalysed transesterification as the former is reported to proceed about 4000 times faster than the latter [2]. The common catalyst employed during alkaline transesterification at industrial level application includes the homogeneous catalysts sodium hydroxide, potassium hydroxide, etc. The use of homogeneous catalyst such as sodium hydroxide and potassium hydroxide has been successful at industrial level for production of biodiesel. However, the biodiesel and glycerine produced have to be purified to remove the basic catalyst and need its separation by washing with hot distilled water twice or thrice [3]

## IV. GLYCERINE AS POTASSIUM SOURCE

The residual crude glycerine from the biodiesel industry corresponds to about 10 to 15% of the total biodiesel mass production. In the lack of any specific legislation indicating how to dispose such residue, much of this by-product is more commonly accumulated in areas of the industrial plants. The expected expansion of the worldwide production of biodiesel will in consequence tend to increase the stock of glycerine [12]. The residual crude glycerine from the biodiesel industry usually contains about 50 mass% of pure glycerine and is rather dark, relatively to the pure glycerine; it needs to be purified for further use in the fine chemistry industry .However this process is expensive and the effluent is usually discarded as waste glycerine by small industries producing biodiesel. Soybean oil is the most widely used for the production of biodiesel. Thus the lower the cost of the soybean production the more interesting would be its industrial use. A conceivable alternative for the agricultural use of crude glycerine from the transesterification of triacylglycerides of bio-oils to produce biodiesel, using potassium hydroxide as catalyst, would be to neutralize the effluent with phosphoric or sulfuric acid. The potassium phosphate or sulphate formed during this step would improve the use of the effluent as fertilizer. Potassium is the second most promptly absorbed macronutrient after nitrogen. The plant nutritional requirements may be variable, depending on in numerous conditions of soil and the plant itself. On average, it assumes an uptake of 81 kg N and 54 kg K to produce 1,000 kg of soybean grains. Some studies have shown that when levels of available potassium in soil are above 60 mg dm-3, the yield responses of the soybean plant to potassium fertilization are usually not significant. Maximum yields of soybeans were reportedly attained with application of 60 kg ha-1; 80 and 120 kg ha-1, if the level of available K in soil was between 16 and 40 mg dm-3 (low content) and between 41 and 70 mg dm-3 (mean content), respectively and 85 and 90 kg ha-1 K2O in case of no-tillage land management. In tropical and subtropical soils, organic matter has a close relationship with other physical, chemical and biological soil properties, chemical among the cation exchange capacity (CEC), is of fundamental importance for maintaining the productive capacity of the soil longer term. Thus, industrial glycerin, as an organic residue, would tend to increase the usually low CEC of tropical soils, to reduce loss of cations, particularly K+, and improve their fertility.

## V. CRUDE GLYCEROL AS POTENTIAL SUBSTRATE FOR BIOGAS

As the biodiesel production is increasing exponentially, the crude glycerol generated in this process has also been generated in a large quantity. Despite the wide applications of pure glycerol in pharmaceutical, food and cosmetic industries, the costs of refining the crude glycerol to a high purity are to high, especially for medium and small biodiesel producers. To improve the economic feasibility of biodiesel industry, new alternate ways of utilization of g-phase have been studied recently. Possibilities such as combustion, co-burning, composting, animal feeding, thermo-chemical conversions and biological conversion have been applied for crude glycerol processing. One of the possible applications is utilization of g-phase as carbon and energy source for microbial growth in industrial microbiology. Microbial conversion of glycerol to various compounds has been investigated recently, with particular focus on the production of 1,3- propanediol, dihydroxyacetone and ethanol. [7, 8] Another option offers biological production of methane from crude glycerol using anaerobic sludge. The advantages include low nutrient requirements, energy savings, generation of low quantities of sludge, excellent waste stabilization and the production of methane. Glycerol is a readily digestible substance, which can be easily stored over a long period. High energy content in g-phase makes it an interesting substrate for anaerobic digestion as well. Considering anaerobic treatment of crude glycerol, potential of its main component glycerol has been well-known for a longer period. Digestion of pure glycerol has been investigated both as a primary substrate, and as an intermediate product of anaerobic degradation of fats. Biodegradation have been carried out using either pure cultures of microorganisms or sludge composed of mixed cultures from waste water treatment plant. Few studies aimed at biogas production from g-phase have also been realized recently. Anaerobic treatment of g-phase as a single substrate was carried out as well as co-processing of crude glycerol with different substrates. Mesophilic anaerobic digestion of crude glycerol was studied in work Lopez et al. (2009). The substrate was previously treated in two different ways: 1) acidification with phosphoric acid and centrifugation (so-called acidified glycerol) or 2) acidification followed by distillation (so-called distilled glycerol). Either granular sludge from anaerobic reactor treating brewery wastewater or non-granular sludge from anaerobic reactor treating urban wastewater was used for inoculation of batch laboratory-scale reactors, having the working volume of one litre.

## VI. BIODIESEL SPENT WASH AS POTASSIUM SOURCE

Biodiesel spent wash is waste water discharged from the biodiesel production units during the process of biodiesel production, where the biodiesel was washed with water to remove the suspended matter and catalysts present in it. About 2 to 3 liters of waste water was produced for production of a litre of biodiesel [11]. The biodiesel spent wash is dark yellowish cream in colour, highly turbid, pungent smelling and has high organic load as seeds are used as a chief raw material in the production, with high levels of chemical oxygen demand, biological oxygen demand, oil, high suspended and dissolved solids, high amount of sodium, nitrogen, phosphorus and potassium content. [10]. To recycle nutrients through land application of biodiesel spent wash requires the use of crops capable of utilization of these nutrients. Industrial effluents rich in organic matter and plant nutrients are finding agricultural use as cheaper way of disposal. Since most of the wastewater is being discharged into the surrounding water bodies [9]

## VII. DE-OILED CAKE IN BIODIESEL PRODUCTION

Present method of utilization of only extracted vegetable oil from the bio-diesel resource results in generation of huge unutilized biomass. In general, 50% (dry weight basis) of the collected fruits of bio-diesel resource are seeds (kernels). Out of these seeds, at the most 35% is converted into vegetable oil and remaining 65% material is rejected as toxic oil seed cake. In short, more than 85% of cultivated bio-resource (seed’s pericoat and oil seed cake) is remaining unutilized in bio-diesel production. This toxic oil seed cake can neither be used as cattle feed nor as a bio-fertilizer for growing plants, due to presence of phorbol ester (a toxic compound). The current annual production of toxic Jatropha oil seed cake alone has been estimated to be about 60,000 tonnes [4]. estimated amount of Jatropha oil seed cake could be a significant source of bio-energy production if it is utilized in a planned manner. Further, waste-to-energy provides a solution to waste management and energy generation. An integrated anaerobic waste vaporization process is an interesting option for energy generation from non-edible oil seed cakes [8]. Anaerobic digestion is considered to be a sustainable bio-conversion technology as it produces biogas a renewable gaseous fuel and it also stabilizes and reduces the volume of waste. As a part of an integrated waste management system anaerobic digestion reduces the emission of greenhouse gases into the atmosphere. The degradation process or digestion of solids in an anaerobic digester takes place in three stages. The first stage is the hydrolysis of particulate and colloidal wastes to solubilise the waste in the form of organic acids and alcohols. The second stage is the conversion of the organic acids and alcohols to acetate, carbon dioxide, and hydrogen. The third stage is the production of gases mostly methane and new bacterial cells or sludge from acetate and hydrogen. In an anaerobic digester a great diversity of bacteria are required to perform phases of hydrolysis, acidogenesis and methanogenesis of the input substrate feed that contains diversified wastes in term of carbohydrates, fats and proteins [6]. Anaerobic digestion of olive oil mill wastewater (OMW) mixed with diluted poultry manure (DPM) in pilot plant reactor of 100 l, containing 40% volatile solids produces biogas at a rate of 1.53 l/d per unit volume of reactor with a methane content of 65% by volume. Co-digestion of wastewater together with local agricultural residues is a sustainable and environmentally attractive method to treat wastes and convert to useful resources. The biogas produced can be used for the generation of heat or electricity; apart from this energy co-digestion results in liquid and solid effluents that are also valuable as they retain all their nutrient constituents (nitrogen, phosphorus, trace elements, etc.). Thus, it can be used as bio-fertilizers and soil organic matter improvers [7]. The major challenge in anaerobic digestion of Jatropha and Pongamia oil seed cakes is lack of inherent bacteria like in cattle dung. Apart from the existing bacteria in a digester, fresh cattle dung continuously adds more bacteria to the digestion system and stabilizes the anaerobic digestion process. However, lack of the inherent bacteria, demands a special attention for operation of digester with non-edible oil seed cakes. Another major drawback of oil seed cake is the presence of long chain free fatty acids, which can destroy the population of bacteria in the digester. Moreover, an appropriate amount of cattle dung with oil seed cake may stabilize the bacterial population. The proximate and ultimate analysis of Jatropha and Pongamia oil seed cakes confirmed that they have rich proportionate of volatile solids content. These oil seed cakes have low non-volatile solids content, higher content of hydrogen and carbon as compared to the cattle dung. The biogas produced from Jatropha and Pongamia oil seed cakes contains 15–20% more methane than the biogas produced from the cattle dung [5].

## VIII. CONCLUSION

The advantage in its usage is attributed to lesser exhaust emissions in terms of carbon monoxide, hydrocarbons, particulate matter, polycyclic aromatic hydrocarbon compounds and nitrited polycyclic aromatic hydrocarbon compounds. The main advantages of biodiesel given in the literature include its domestic origin, its potential for reducing a given economy's dependency on imported petroleum, biodegradability. The process of biodiesel production is predominantly carried out by catalysed transesterification. Besides desired methyl esters, this reaction provides also a few other products, including crude glycerol, oil-pressed cakes and washing water. Although their composition widely varies depending on the parameters and substrates used for biodiesel production, all these by-products provide valuable feedstocks for biogas generation. Washing water from biodiesel purification is also a promising material for anaerobic degradation, considering the high content of readily degradable organic substances. Such usage of spent wash and by-products from biodiesel production will lower down the treatment and provide economic benefits.

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