A COMPARISON OF BIODIESEL PURIFICATION METHODS

CJ Schabort, PJ van der Walt, S Marx
School of Chemical and Minerals Engineering, North-West University, Potchefstroom, South Africa
Tel.: +27 18 299 1760 Fax: +27 18 299 1535 E-mail: corneels.schabort@nwu.ac.za

ABSTRACT: The purification of biodiesel is of cardinal importance to ensure the final product meets industry standards. This final step in the production stage contributes a large portion of the cost attributed to biodiesel production. The aim of this study was to compare four biodiesel purification methods and the energy required to provide a fuel that meets specifications. Major contaminants (water and soap) and fuel properties (oxidative stability) were investigated and compared for the four purification methods. These methods were wet washing with thermal drying and dry washing with Magnesol™ D-Sol, Purolite™ PD206 and sunflower husk ash. The dry-wash methods proved to be more effective in the removal of contaminants and were less energy intensive than traditional wet washing. Dry washing costs were shown to be significantly lower than for traditional wet washing.

Keywords: biodiesel, biofuel, sunflower, transesterification

1 INTRODUCTION

The drastic increases in global energy demand, together with the rapid depletion of fossil fuel resources, stress the need for vigorous research in the field of renewable energy to ensure future of energy generation.

Bio-fuels, including bio-ethanol, biodiesel and bio-gas, have enormous potential in the field of alternative energy and the complete renewability of these sources ensures the viability thereof. Bio-fuels will not be able to substitute fossil fuels completely, but can serve as a complimentary source. The main hurdle for biodiesel as an alternative fuel is the cost of production. A major cost aspect in the biodiesel production process is the washing, drying and purification methods utilized to ensure that the final product is within industry standards [1].

1.1 Biodiesel Production Methods

Biodiesel can be produced using a wide range of chemical reactions like pyrolysis (thermal cracking), micro-emulsion and transesterification [2]. Biodiesel is often produced by the chemical process, transesterification. This is the reaction of a lipid with alcohol to form esters and glycerol as a by-product [1]. This reaction takes place in three stages and catalysts are usually preferred. The most common catalyst is an alkaline catalyst like sodium hydroxide or potassium hydroxide [1].

The process of transesterification is described by the following equations, with triglycerides (TG), diglycerides (DG), monoglycerides (DG) and Fatty Acid Methyl Esters (FAME) [1]:

$$\text{TG} + \text{MeOH} \leftrightarrow \text{DG} + \text{FAME} \quad (1.1)$$

$$\text{DG} + \text{MeOH} \leftrightarrow \text{MG} + \text{FAME} \quad (1.2)$$

$$\text{MG} + \text{MeOH} \leftrightarrow \text{FAME} + \text{glycerol} \quad (1.3)$$

These reactions take place in an alkaline environment which acts as a catalyst to lower the activation energy.

1.2 Feedstock

The ideal feedstock for usage in biodiesel production should have a high triglyceride content. Currently there are more than 350 oil-bearing crops identified as potential sources for the production of biodiesel [3]. The main factors to be taken into consideration in determining an optimal feedstock is the availability of the particular feedstock, the cost thereof, as well as the possible biodiesel conversion. Availability of the feedstock may be seasonal and can vary due to climate and soil conditions. The acquisition of the feedstock can represent up to 75% of the cost of production, therefore an inexpensive feedstock should be used.

First generation feedstocks, such as sunflower and rapeseed oils, are produced from edible sources and therefore contribute to the food versus fuel debate. Second generation feedstocks include animal fats and tobacco seeds that are inedible and do not affect food security [3]. The combination of first and second generation feedstocks will not provide sufficient biodiesel volumes to satisfy the global energy demand [3]. Other debates such as the fuel versus fodder, fuel versus chemicals and the use of water as a reactant or purification method have become serious concerns in bio-fuel production.

The water used in the biodiesel purification step and the feedstocks used contribute to environmental concerns. The most popular feedstock for biodiesel production is currently rapeseed (84%), followed by sunflower oil (13%), palm oil (1%) and soybean oil (<1%) [3].

Sunflower oil consists of a wide range of fatty acids, from C6:0 to C24:1 and is obtained by extracting oil from sunflower seeds mechanically, chemically or enzymatically [4]. The sunflower oil used for the production of biodiesel can be used oil that has been filtered thoroughly and neutralized.

1.3 Alcohol

Alcohol is used as a reactant and serves as a solvent for the catalyst. A short chain alcohol, usually methanol or ethanol, is preferred as this will lead to a better yield with less side reactions [1]. Methanol is preferred in laboratory use as this gives a good yield, is relatively inexpensive and relatively safe. Furthermore, methanol produces higher biodiesel yields than ethanol [5]. South African biodiesel standards do not allow FAEE in the fuel mixture and the use of ethanol will result in the formation of ethyl esters [14].

Methanol is added to the experimental setup in excess with ratios ranging from 5:1 to 9:1 [6] although a stoichiometric amount of 3 moles methanol per mole oil is sufficient [7]. This will ensure less saponification, deliver a better yield and shorten the reaction time [8]. However, too large an excess can lead to a higher solubility of glycerol, which interferes with the separation of the products. This will lead to a lower conversion [6].

A methanol to oil ratio of 6:1 is preferred [1]. The excess methanol will ensure a rapid reaction rate [8]. After completion of the reaction, the excess methanol is removed by heating the mixture to above the boiling point of methanol which is 65°C [9].

1.4 Catalyst

Minimizing catalyst usage whilst maximizing the biodiesel overall yield is a challenge faced by all biodiesel manufacturers [10]. A wide variety of catalysts are used in the industrial process of biodiesel production such as solid catalysts and alkoxide catalysts.

The process of transesterification can take place in acidic or alkaline environments. The alkaline environment is usually preferred and therefore a catalyst such as sodium hydroxide or potassium hydroxide is usually used [4]. A by-product of this reaction is glycerol. The unspent catalyst is neutralized with a low concentration acidic solution.

Sodium hydroxide and potassium hydroxide are supplied in the form of flakes and have to be dissolved in the methanol before used as a reactant. Potassium hydroxide has the added benefit, if used, that after the neutralization reaction with sulphuric acid, it produces potassium sulphate as a by-product. This can easily be separated and sold as a fertilizer [11]. Potassium hydroxide is more soluble in methanol, which may further shorten the reaction time.

The preferred catalyst concentration is normally 1wt% of the oil [9], however concentrations ranging from 0.3wt% to 3wt% have been reported [7].

1.5 Reaction conditions

Temperatures for the transesterification reaction may vary between 45°C and 70°C however the optimal temperature is 65°C for alkaline catalysed transesterification. Reaction times may vary according to the amount of alcohol in the reaction mixture, although 1h is the accepted reaction time [5], [6], [7], [12].

1.6 Purification

Biodiesel purification is generally divided into two categories, namely wet washing and dry washing. Wet washing is the process where biodiesel, after the glycerol is removed, is washed with distilled water at a slightly elevated temperature of 55°C [13]. This removes soap and evenly distributes the remaining catalyst between the two phases. The elevated temperature also removes a fraction of methanol. The biodiesel is phase separated in a separator funnel. The top phase contains the biodiesel, which is then thermally dried at a temperature of 100°C. This is done for a minimum time of one hour.

Dry washing entails the addition of ion exchange resins such as Purolite™ PD206 or Eco2Pure™, although absorbers such as Magnesol™ D-Sol are also common for dry washing purposes. After the removal of the glycerol, the biodiesel is exposed to the resin or absorbing agent at a temperature of 65°C. These compounds are developed exclusively for biodiesel purification and are effective in the removal of soap, water, catalyst and other contaminants.

Magnesol D-Sol™ is a synthetic inorganic absorber that consists of magnesium silicate and anhydrous sodium sulphate [15]. It is produced by the Dallas Group and has an average particle size of 60μm [15]. Magnesol™ is effective for the removal of impurities such as soap, water, catalyst and glycerol from biodiesel [15]. This compound is polar in nature and therefore has an affinity for polar compounds such as water, methanol, glycerol and catalyst [16].

Purolite PD206™ is an organic ion-exchange resin that has been specifically developed to remove impurities such as water, soap, salt, glycerol and unspent catalyst [13]. Purolite PD206™ removes soap by substituting the sodium or potassium ion in the soap compound for a hydrogen ion, effectively producing a FFA molecule [17]. The ASTM maximum for soap in biodiesel is 66ppm, whereas the maximum FFA content is 2500ppm [15]. Therefore the transformation of soap into FFA is permissible.

Rice husk ash has been used successfully to dry-wash biodiesel [16]. In accordance with this, the absorbance capabilities of sunflower husks and sunflower husk ash were investigated as this is a more readily available material in South Africa.

A study done by Faccini *et al.* [11] compared dry washing methods. The result of this study is summarised in Table I. It is visible that Magnesol™ with a 1wt% concentration provided the lowest water and soap contents for the biodiesel samples.

Table I: Results from Faccini *et al.* [11]

Samples	Water [mg/kg]	Soap [ppm]
Not Purified	1300	1670
Wet Washing	1400	158
Magnesol™ 1%	500	61
Magnesol™ 2%	800	61
Purolite™ 1%	1200	213
Purolite™ 2%	1100	243

1.7 Purification Energy Consumption

Heating and agitation during the purification process is energy intensive and add significantly to the cost of biodiesel production. For thermal drying, energy is added to heat until the mixture reaches a temperature of 65°C. At this temperature methanol is evaporated which requires energy. After the evaporation the remaining biodiesel and unreacted oil is heated to 100°C to evaporate the remaining water. The evaporation step is also energy intensive.

Theoretically, dry washing should consume less energy, as water is not evaporated and the biodiesel is only heated to 70°C.

1.8 Biodiesel standards

According to SANS 1935 [14], the industry standard for water content is 50ppm. No standards are given for biodiesel soap content in SANS 1935, however ASTM does limit the soap content to 66ppm if a KOH catalyst is used [15]. The oxidative stability has a SANS 1935 standard of 6h [14].

2 MATERIALS AND METHODS

2.1 Materials

Sunflower oil was used as a feedstock to produce biodiesel via the transesterification process. Three dry washing methods were compared, each with a separate absorber or ion-exchange resin.

2.2 Chemicals

The catalyst used during the transesterification process was 1wt% (catalyst to oil ratio) of potassium hydroxide [9]. Potassium hydroxide was chosen as the alkaline catalyst due to the high yields obtainable over a vast array of feedstocks [12].

Methanol was preferred over ethanol for biodiesel production as methanol is less expensive. According to SANS 1935 biodiesel in South Africa may not contain any FAEE. Ethanol produces FAEE while methanol provides FAME. Methanol however is not as soluble in oil as ethanol due to the higher polarity of this alcohol. This does not adversely affect the yield as methanol delivers higher yields than ethanol [5].

2.3 Experimental methods

2.3.1 Biodiesel production

Two batches of biodiesel were produced with the sunflower oil feedstock with identical methods. The oil (300g) was measured into a three neck round bottom flask. The flask was equipped with a thermometer, a condenser to prevent methanol evaporation and a rubber plug.

A heat jacket was used to maintain the temperature at 65°C [1] with a magnetic stirrer to ensure sufficient agitation (300rpm). The KOH was dissolved in methanol at a concentration of 1wt% catalyst to oil. Methanol was added to an oil molar ratio of 6:1 [4] and the mixture was allowed to react for one hour [4]. After the reaction was completed the biodiesel was left in a separating funnel to phase separate from the glycerol.

2.3.2 Wet washing

The top phase from the separating funnel (biodiesel) was washed with distilled water and left to phase separate for a second time. The bottom phase from the second separating funnel was removed and discarded and the top phase (biodiesel) was dried in an oven.

Temperatures of 70°C, 90°C and 100°C were chosen to evaporate the residual water. The temperature of 70°C was chosen to provide a more accurate energy comparison between the dry and wet washing alternatives, as all dry washing was done at 70°C. Drying time was varied between 15min and 90min to provide accurate drying curves with regards to time.

2.3.3 Dry washing

The top phase from the first separating funnel in section 2.3.1 was dry-washed by using Magnesol™ D-Sol, Purolite™ PD206 and sunflower husk ash. Identical methods were used to compare these three alternative methods.

The biodiesel was poured into a beaker equipped with a magnetic stirrer. The setup was performed on a heat plate, set to a temperature of 70°C to ensure that the majority of the methanol has evaporated. Varied concentrations of the dry washing compounds were added to the biodiesel. For the Magnesol™ and Purolite™, concentrations of 0.5wt%, 1wt% and 1.5wt% were chosen [13]. Sunflower husk ash was investigated at concentrations of 1.5wt%, 2wt% and 3wt%. At varied time intervals, samples were extracted from the mixture and filtered using 20µm syringe filters.

2.4 Analytical Methods

The moisture content of the biodiesel samples was determined with the Karl Fischer Coulometer (KFC). Ester content and the presence of methanol were measured by gas chromatography (GC).

The soap content was obtained with a hydrochloric acid titration. 10g biodiesel was dissolved in 100mL isopropyl alcohol after which bromophenol blue was added until the colour of the solution turned blue [17]. Measured amounts of 0.01N hydrochloric acid was titrated into the solution until the colour turned yellow (pH = 3). The soap content in ppm is equal to the product of the volume hydrochloric acid added (mL) and the catalyst factor. The catalyst factor in the case of KOH is 320 [17].

The energy usage for all biodiesel purification and drying methods was determined by means of the power rating of the equipment used. Energy consumed by the equipment for heating purposes was calculated. The power rating of the oven is 1000W and since it makes use of an on-off system, the power used is independent of temperature. The power rating for the hot plate is 825W.

3 RESULTS AND DISCUSSION

3.1 Biodiesel composition

Biodiesel samples were prepared using wet and dry washing methods. The average moisture and soap content for the wet washing samples were 756±51ppm and 113±7ppm respectively.

3.2 Moisture removal

In Figure 1 the water removal efficiency of the wet washed biodiesel samples that were dried thermally, is shown.

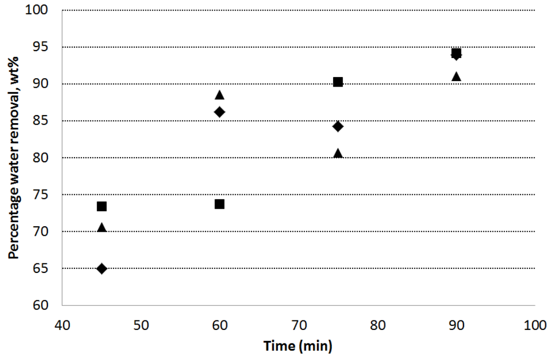

Figure 1: Water removal efficiency of wet washed biodiesel dried thermally at 100°C, 90°C and 70°C. (◆ 100°C, ■ 90°C, ▲ 70°C)

In Figure 1 the increase in moisture removal is visible over the 90min period. The moisture content limit of 50ppm (94% moisture removal) was reached after 90min at the temperatures of 90°C and 100°C. The moisture content after 90min at 100°C was 46±7ppm, while it was 44±7ppm for the sample that was dried at 90°C. It was not possible to sufficiently dry the biodiesel sample at 70°C and 67±10ppm moisture remained in the biodiesel.

In Figure 2, the water content of the biodiesel dry washed with Magnesol™ D-Sol is shown.

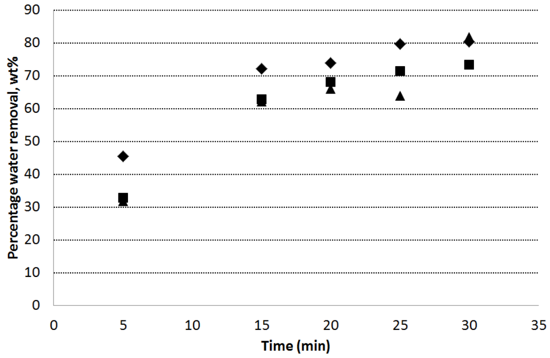

Figure 2: Water removal efficiency content of biodiesel dry washed with Magnesol™. (◆ 0.5 wt%, ■ 1 wt%, ▲ 1.5 wt%)

From Figure 2 it can be seen that Magnesol™ D-Sol is able to reduce the water content to below the acceptable limit of 50ppm within 30min, which is a much shorter time than was the case with thermal drying. Figure 3 shows the water content of biodiesel dry washed with Purolite™ PD206.

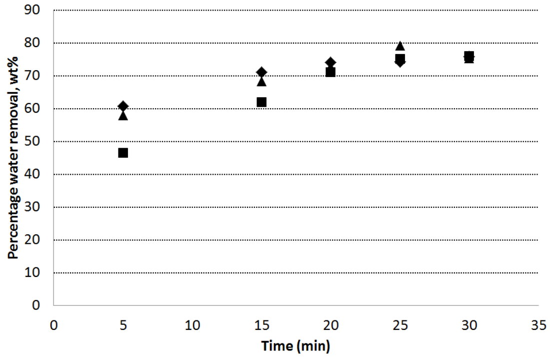

Figure 3: Water removal efficiency content of biodiesel dry washed with Purolite™ PD206. (◆ 0.5 wt%, ■ 1 wt%, ▲ 1.5 wt%)

Figure 3 illustrates the decrease of water content over a 30min period for Purolite™ PD206. These resin concentrations reduced to moisture content to below the standard of 50ppm within 15min. Figure 4 depicts the water content of biodiesel after dry washing with sunflower husk ash.

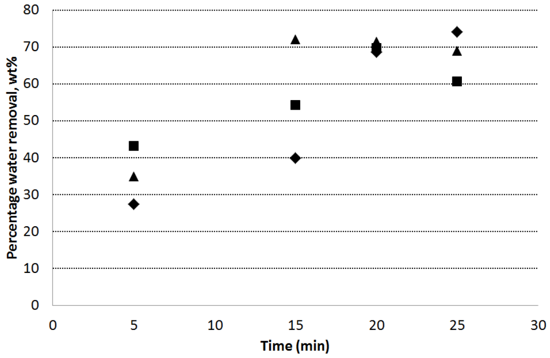

Figure 4: Water removal efficiency content of biodiesel dry washed with Purolite™ PD206. (◆ 0.5 wt%, ■ 1 wt%, ▲ 1.5 wt%)

From Figure 4 it is evident that sunflower husk ash does succeed in the reduction of moisture content to below the industry standard of 50ppm after 20min.

3.3 Soap removal

Traditional wet washing reduced the soap content to 113±7ppm. This is 72% higher than the industry standard of 66ppm. The soap content of the biodiesel after dry washing with Magnesol™ D-Sol is shown in Figure 5.

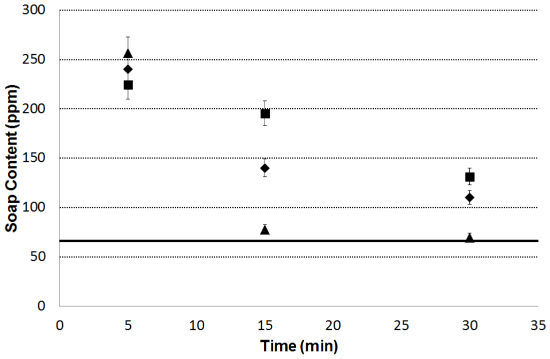

Figure 5: Soap content of biodiesel dry washed with Magnesol™ (■ 0.5wt%, ◆ 1wt%, ▲ 1.5wt%)

The soap content of the biodiesel was reduced by all of the concentrations of the Magnesol™ D-Sol, but only the 1.5wt% was able to reduce the concentration to below the standard of 66ppm. With a 1.5wt% Magnesol™ concentration, the biodiesel sample reached a soap content of 59±4ppm within 15min. The higher concentration Magnesol™ was able to absorb higher amounts of soap.

Figure 6 shows the soap content of biodiesel after dry washing with Purolite™ PD206. Only the 1.5wt% resin reduced the soap content to a final concentration below 66 ppm.

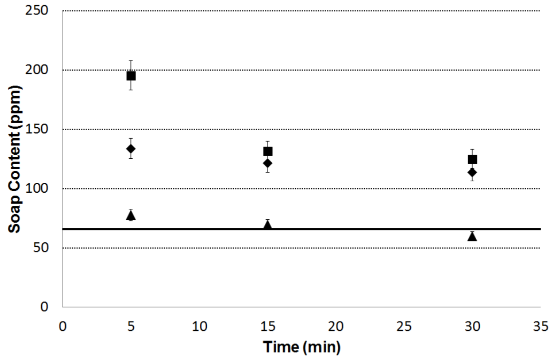

Figure 6: Soap content of biodiesel dry washed with Purolite™ (■ 0.5wt%, ◆ 1wt%, ▲ 1.5wt%)

Figure 7 portrays the soap content of biodiesel dry washed with sunflower husk ash.

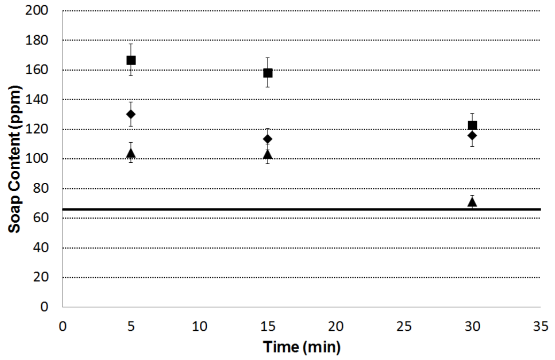

Figure 7: Soap content of biodiesel dry washed with sunflower husk ash (■ 1.5wt%, ▲ 2wt%, ◆ 3wt%)

From Figure 7 it is visible that none of the sunflower husk ash concentrations was able to reduce the soap content below the 66ppm standard. The best soap removal was achieved using a 2wt% ash concentration, but it does not have the same absorptive capabilities of Magnesol™ and Purolite™.

3.4 Energy consumption and purification cost

The energy required to elevate the temperature of the biodiesel to 100°C in the case of thermal drying, and to 70°C in the case of the dry washing methods, is shown in Table II.

Table II: Energy required to reach desired temperature

Method	Residual water [mg/kg]	Residual soap [ppm]	Energy required [kJ]
Wet washing	44	113	5,400
Magnesol™	27	60	1,800
Purolite™	37	69	1,800
Sunflower husk ash	38	73	1,800

The actual cost of using the various methods are shown in Table III, either showing the electricity cost for thermal heating, or showing the cost of using the drying agents. The sunflower husk ash is excluded, as the ash is not able to sufficiently reduce the soap content to within specification.

Method	Cost [€/l biodiesel]
Wet washing	0.05
Magnesol™	0.03
Purolite™	0.02
Sunflower husk ash	

4 CONCLUSIONS

It can be concluded that traditional wet washing is not only more expensive than dry washing methods, but also not able to remove the soap to below the industry standard of 66ppm. The energy required to remove the water used in the washing stage is however around 70% higher than the energy consumed during the dry washing processes. Furthermore, a washing period of 90min is required, which is much longer than is the case with dry washing methods.

Magnesol™ D-Sol was highly effective in removing water and soap. These contaminants were removed to the extent where the biodiesel was well within specification with regards to soap and moisture content. Magnesol™ at a concentration of 1.5wt% and a period of 20min will ensure biodiesel within specification with regards to soap and water content.

Purolite™ PD206 is a highly effective contaminant remover and dry washing resin. The water content after 20min was consistently lower than 50ppm. This ion exchange resin performed well in the removal of soap, but was still slightly above the specified 66ppm. The best result with this resin was obtained with a concentration of 1.5wt%. Even though Purolite™ is slightly less expensive than Magnesol™, it took 10min longer to reach the optimal water and soap content. This may be due to the fact that, other than Magnesol™, Purolite™ relies on an ion exchange reaction. This reaction may require activation energy or the reaction may not be as rapid as the absorption process the Magnesol™ utilises.

The sunflower husk ash succeeded in reducing the water content to below the specified 50ppm. Although the specification for soap was not met, the sunflower husk ash did reduce the soap content significantly.

Dry washing thus proved to be more time efficient, cost efficient and purification efficient than traditional wet washing.

5 REFERENCES

[1] C.C. Enweremadu, M.M. Mbarawa, Technical aspects of production and analysis of biodiesel from used cooking oil: A review, Renewable and Sustainable Energy Reviews, (2009), pag. 2206.
[2] A.E. Atabani, A.S. Silitonga, I.A. Badruddin, Mahlia, T.M.I., H.H. Masjuki, S. Mekhlief, S. A comprehensive review on biodiesel as an alternative energy source and its characteristics, Renewable and Sustainable Energy Reviews, Vol. 1, No. 16, (2012), pag. 2070.
[3] K. Warner, B. Vick, L. Kleingartner, R. Isaak, K. Dorof, Compositions of sunflower, nusun and high oleic sunflower oils, (2009).
[4] A. Demirbas, Production of biodiesel fuels from linseed oil using methanol and ethanol in non-

catalytic SCF conditions, Biomass and Bioenergy, Vol. 1, No. 33, (2009), pag. 113.
[5] M. Berrios, J. Siles, M.A. Martin, A. Martin, A kinetic study of the esterification of free fatty acids (FFA) in sunflower oil, Fuel, Vol. 1, No. 86, (2007), pag. 2383.
[6] A. Demirbas, Progress and recent trends in biodiesel fuels, Energy Conversion and management, Vol. 1, No. 50, (2008), pag. 14.
[7] A. Porte, R. Schneider, J.H. Kaercher, R. Klamt, W.L. Scmatz, W. da Silva, W. Filho, Sunflower biodiesel production and application in family farms in Brazil, Fuel, Vol. 1, No. 89, (2010), pag. 3718.
[8] N. Dunford, Biodiesel production techniques, (2010).
[9] B. Sims, Catalysing biodiesel growth, Biodiesel Magazine, (2012), pag. 8.
[10]T. Bryan, Absorbing it all, Biodiesel Magazine, (2010).
[11]C. Faccini, M. da Cunha, M. Moraes, L. Krause, M. Manique, M. Rodrigues, E. Benvenutti, E. Caramao, Dry Washing in Biodiesel Purification: a Comparitive study, Journal of the Brazil Chemical Society, (2011), pag. 559.
[12]South African National Standards, SANS 1935:2004, (2004).
[13]J. van Grepen, K. Menges, Evaluation of Magnesol R60 as an alternative to water washing during biodiesel production, (2004).
[14]J.W. Kram, Cleaner and Clearer. Biodiesel Magazine, (2004).
[15]Utah Biodiesel Supply, (2009), [online], http://www.utahbiodieselsupply.com
[16]M. Manique, C. Faccini, E. Benvenutti, E. Caramao, Rice husk ash as an adsorbent for purifying biodiesel from waste frying oil, Fuel, (2012), pag. 56.
[17]U. Rashid, F. Anwar, Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil, Fuel, Vol. 1, No. 87, (2007), 265