Indo American Journal of Multidisciplinary Research and Review
ISSN: 2581 - 6292 / Website: www.iajmrr.com

IMPROVING THE YIELD OF BIODIESEL FROM KARANJA OIL TRANSESTERIFICATION USING NANO CATALYST

M. Muthuprasanth*, Dr. S. Balachandran**,
Dr. S. Babu*** & Dr. M. Govindaraj****

* PG Scholar, Department of Mechanical Engineering, PSG College of Technology, Coimbatore, Tamilnadu
** Professor , Department of Mechanical Engineering, PSG College of Technology, Coimbatore, Tamilnadu
*** Assistant Professor , Department of Mechanical Engineering, PSG College of Technology, Coimbatore, Tamilnadu
**** Assisitant Professor, Department of Chemistry, Thanthai Hans Roever College, Perambalur, Tamilnadu

Cite This Article: M. Muthuprasanth, Dr. S. Balachandran, Dr. S. Babu & Dr. M. Govindaraj, "Improving the Yield of Biodiesel from Karanja Oil Transesterification Using Nano Catalyst", Indo American Journal of Multidisciplinary Research and Review, Volume 3, Issue 2, Page Number 1-6, 2019.

Abstract:

Biodiesel is a promising alternating environmentally benign fuel to mineral diesel. For the development of easier transesterification process, stable and active heterogeneous mixed metal oxide of TiO_2–K nanocatalyst was synthesized and exploited for the karanja oil transesterification process. The synthesized catalyst was characterized by XRD, and HRTEM studies for their structural characteristics. It was found that TiO_2–K nanocatalyst exhibits good catalytic activity and the catalytic performance was greatly depends on (i) catalyst concentration (ii) methanol to oil molar ratio (iii) reaction temperature and (iv) reaction time. A highest 86% of conversion was obtained at the optimum reaction parameters with 4% of catalyst loading and 7% potassium loading. The TiO_2–K nanocatalyst shows good catalytic performance, which could be a potential candidate for the large-scale biodiesel production from Karanja oil at the reduced temperature and time.

1. Introduction:

Biodiesel fuel (BDF) is well known as a renewable, nontoxic, biodegradable, and environment-friendly that can substitute petro-diesel perfectly which can be used directly or as diesel mixture in engines with little changes. Biodiesel can be produced through transesterification of vegetable oils and fats with methanol in the presence of a suitable catalyst. Any type of feedstock that contains free fatty acids and/or triglycerides such as vegetable oil, waste oil, animal fats, and waste greases could be converted into biodiesel. In conventional method of transesterification reaction (homogeneous catalysts) number of purification steps are needed to meet the stipulated qualities (Chen et al., 2010) thereby increase the capital and operating costs (Canakci, 2007). Therefore, for the development of an environmentally benign process and the reduction of the production cost, a new process using heterogeneous catalyst should be introduced.

Numerous investigations have been conducted on the BDF production using heterogeneous base catalysts as they offer higher catalytic activity than solid acid catalysts (Abbaszaadeh et al., 2012). Metal oxides CaO, SrO, MgO, etc., mixed metal oxides Ca/Zn, Ca/Mg, etc., alkali-doped metal oxides CaO/Al_2O_3, MgO/ Al_2O_3, Li/CaO, etc., Al2O3-supported alkali metal oxide catalysts Na/NaOH/c-Al_2O_3, K2CO3/Al_2O_3 hydrotalcites, and K/Ca/Al/Fe_3O_4 magnetic composites were used as solid base catalysts. Although these heterogeneous catalysts have some advantages such as easier catalyst separation and pollution reduction, most of them have limitations such as they required high reaction temperature (>170 _C), long reaction time (>24 h) and low catalytic stability with significant leaching of catalyst components to the deactivation of the catalyst. The use of nanocatalyst provides higher catalytic activity, easier to separate and reusable, simple operational procedures, and regenerates of less pollution (Hu et al., 2012).

The catalyst was prepared by impregnation method and the catalytic activity towards the transesterification of karanja oil (conversion of the methyl esters) was examined. X-raydiffraction (XRD), Besides the biodiesel and catalysts characterization, the effect of reaction variables such as methanol to oil molar ratio, reaction time, reaction temperature, and catalyst loading on the conversion of methyl esters were also investigated.

Karanja is a medium sized tree is found almost throughout India. The common name of the oil is Karanja Seed Oil and the botanical name is Pongamia glabra of Leguminaceae family. Pongamia is widely distributed in tropical Asia and it is nonedible oil of Indian origin. It is found mainly in the Western Ghats in India, northern Australia, Fiji and in some regions of Eastern Asia. .The plant is also said to be highly tolerant to salinity and can be grown in various soil textures viz. stony, sandy and clayey. Karanja can grow in humid as well as subtropical environments with annual rainfall ranging between 500 and 2500 mm. This is one of the reasons for wide availability of this plant species. The tree bears green pods which after some 10 months change to a tan colour. The pods are flat to elliptic, 5-7 cm long and contain 1 or 2 kidney shaped brownish red kernels. The yield of kernels per tree is reported between 8 and 24 kg. .The kernels are white and covered by a thin reddish skin. The composition of typical air dried kernels is: Moisture 19%, Oil 27.5%, and Protein 17.4%. The present production of karanja oil approximately is 200 million tons per annum. The time needed by the tree to mature ranges from 4 to 7 years and depending on the size of the tree the yield of kernels per tree is between 8 and 24 kg.

2. Preparation and Characterization:

2.1. Catalyst Preparation:

Refined karanja oil was purchased from local market. Methanol (>99% purity) was of analytical grade purchased from E-Merck, India and was used as received without purification.

Initially the Titanium oxide (anatase) was mixed with required amount of water, The amount of potassium loaded onto Titanium oxide were 2, 5,7,10, and 12 w/w% by using KNO_3 (Merck) as the potassium precursor. Then the support was mixed to the previous solution and heated slowly to evaporate the excess of water. The magnetic stirrer speed was maintained 500 rpm and the mixture was stirred continuously at 100 ˚C to achieve the homogeneity until the mixture becomes paste-like precursor. The precursor was kept oven at 120 ˚C to remove the water. After, this the K-TiO_2 was milled to produce fine particles. Finally the powder was calcinated in a furnace at 500 ˚C for 2hrs and cooled for 8 hours

2.2 Catalyst Characterization:

The powder X-ray diffraction (XRD) pattern for the synthesized nanocatalyst samples were recorded using a diffractometer and the obtained peaks are shown in figure 1, which is compared with the standard curve of anatase, shown in figure 2. The phases present in the samples were identified with the help of JCPDS (Joint Committee of the Powder Diffraction Standard) database files. The XRD patterns of TiO2–K nanocatalysts show the formation of hexagonal KNO_3 (JCPDS No.: 89-1397) and Tetragonal TiO2 (JCPDS No.: 89-6975) phases clearly indicating that KNO_3 and TiO2 were partially present in the form of hexagonal and tetragonal crystallites. The XRD patterns exhibits the formed metal oxide- nitrate catalyst was possibly the mixed oxide and nitrate of a Ti and K and did not form any specific structures but they were present as separate oxides and nitrates respectively. On the other hand the characteristic peak of KNO_3 was almost changed with respect to Ti substitution

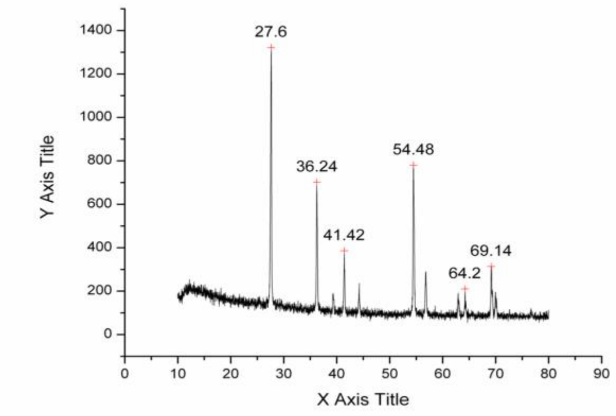


Figure 1: XRD analysis of prepared K-TiO_2

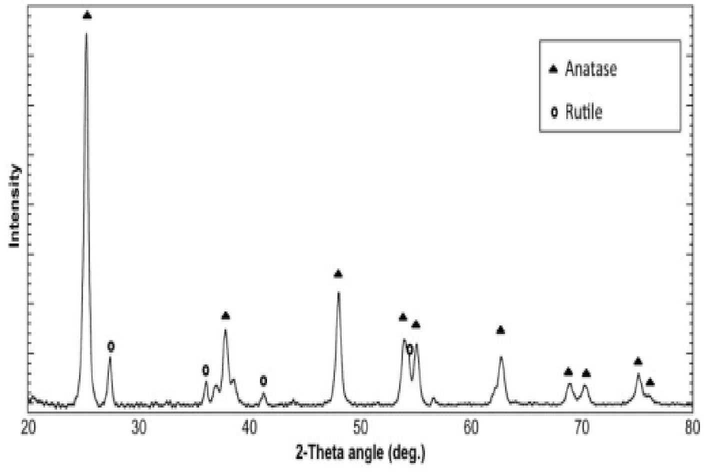


Figure 2: XRD analysis of standard TiO_2 anatase

High-resolution transmission electron microscopy (HRTEM) is an imaging mode of the transmission electron microscope (TEM) that allows for direct imaging of the atomic structure of the sample. The prepared sample was analyzed using HRTEM technique and the electrons were focused on the catalyst at 50nm scale and the result is shown in figure 3. The potassium particles were adsorbed on the surface of Titania, which is evident from the distinct colouration at the outer periphery. The particles were found to be spherical in shape and from the scaling, average particle size were found to be 200nm

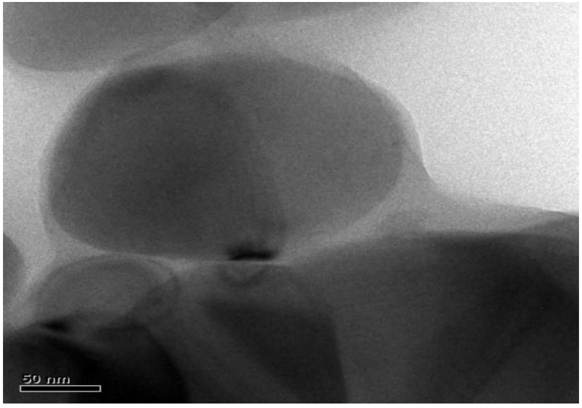


Figure 3: HRTEM analysis of prepared K-TiO_2 at 50nm

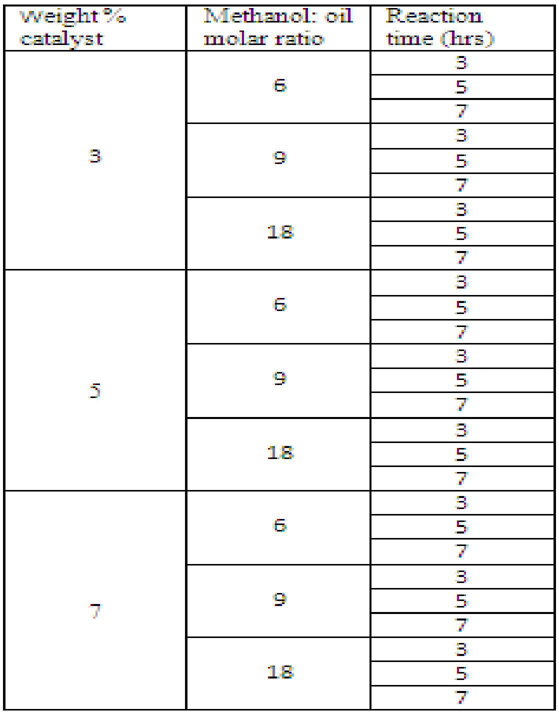
3. Experiments:

3.1 Experimental Setup:

The experimental setup consists of a round bottom flask, connected to a condenser. The condenser is in turn connected to a water bath with a motor, for forced water circulation. Water circulation is required to condense the evaporating gases and to readmit them into the round bottom flask. The round bottom flask and condenser is placed over an oil bath, filled with silicon oil for better heat transfer and stability. The entire setup is placed over a magnetic stirrer with heater arrangement. Magnetic pellet was used to achieve the stirring action. Constant stirring at 500rpm was achieved using the magnetic pellet and stirrer. The experimental setup is shown in figure 4.

Figure 4: Experimental setup

3.2 Optimization Procedure:



Weight % catalyst	Methanol: oil molar ratio	Reaction time (hrs)
3	6	3
		5
		7
	9	3
		5
		7
	18	3
		5
		7
5	6	3
		5
		7
	9	3
		5
		7
	18	3
		5
		7
7	6	3
		5
		7
	9	3
		5
		7
	18	3
		5
		7

Table 1: First optimization

Four parameters have to be optimized in the present work, to achieve maximum yield. The parameters to be optimized are as follows

- Percentage of catalyst loading
- Reaction time
- Methanol to oil ratio
- Percentage of potassium loading

The first three parameters were first optimized by conducting 3^3= 27 experiments and a numerical search technique. The most optimal conditions were found out. Using this fourth parameter was optimized. The list of experiments conducted is shown in table 1. From the below set of experiments, the yield of biodiesel was calculated in each case and the reaction resulting in the highest yield was taken as optimality for reaction time and methanol: oil molar ratio. The optimized time and molar ratios were later used to optimize the percentage catalyst loading, among 2, 3, 4, 5, and 7%. Finally the three parameters that were optimized so far were used to optimize the percentage potassium loading among 2, 5, 7, 10, and 12%.

3.3 Pre Experiment Calculation:

The experiment was done with 50 cc of karanja oil, and all the required parameters are now calculated using this volume.

Quantity of Karanja oil taken= 50cc
Density of oil 924kg/m^3 = 0.92g/cc
Mass=volume* density 50*0.92 = 46.20g

Catalyst loading
Catalyst loading for weight percentage 3%, 5%, 7%.

For 3%, required amount of catalyst =(3/100)*46.2
=1386mg
For 5%, required amount of catalyst =(5/100)*46.2
=2312mg
For 7%, required amount of catalyst = (7/100)*46.2
=3234mg

Methanol molar mass = 32 g/mol
Density of methanol = 900 kg/m^3 =0. 9g/cc
Molar methanol to oil ratio required is 1:6, 1:9, 1:18
Required amount of methanol for 1:6
Molar mass of Karanja oil = 892g/mol
Moles of oil = 46.20/892 = 0.051
Moles of methanol = 0.051*6 = 0.306
Methanol amount = 0.306*32 = 9.79g
= 9.79/0.9 = 10.88cc
For 1:9 ratio, required volume = 16.32cc
For 1:27 ratio, required volume = 32.64cc
Time of reaction 3hrs, 5 hrs, 7 hrs
Temperature of reaction 60°C

4. Results & Discussions:

4.1 Optimization of Reaction Time & Methanol: Oil Molar Ratio:

Initially transesterification was done with KOH base catalyst with 1% catalyst weight, molar ratio 9, reaction temperature 60°C and reaction time of 1.5 hours, to obtain the maximum yield (venkata ramesh, et.al), and the yield obtained on weight basis was 77.6%.

The experiments were conducted with 3 variables, namely catalyst weight %, methanol: oil molar ratio and reaction time as shown in table 1. Totally 27 experiments were conducted and the yield of biodiesel was calculated by weight method, given by the formula

$$\text{Yield \%} = \frac{\text{mass of biodiesel produced X 100}}{\text{mass of oil}}$$

The results showed a maximum yield at a reaction time of 5 hours and a molar ratio of 9. The results were consistent in all cases and so it was concluded that the optimal reaction time was 5 hours and the optimal methanol: oil ratio was 9. The results of the above experiments are shown in figure 4.1, 4.2, 4.3.

In each case the molar ratio 9 and reaction time 5 hours, showed the highest peak. Yield was the highest in molar ratio 9 and lowest in molar ratio 18. Similarly yield was highest in 5 hours and lowest in 7 hours. The maximum yield obtained from the experiments was 83.3% at 3% catalyst weight, 9 molar ratio and reaction time of 5 hours. The conclusion here is that the optimal value of molar ratio is 9 and optimal reaction time is 5 hours.

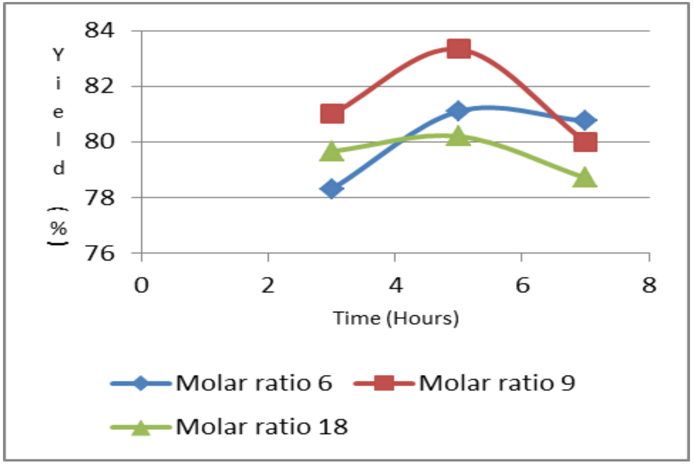


Figure 4.1: Results for 3% weight

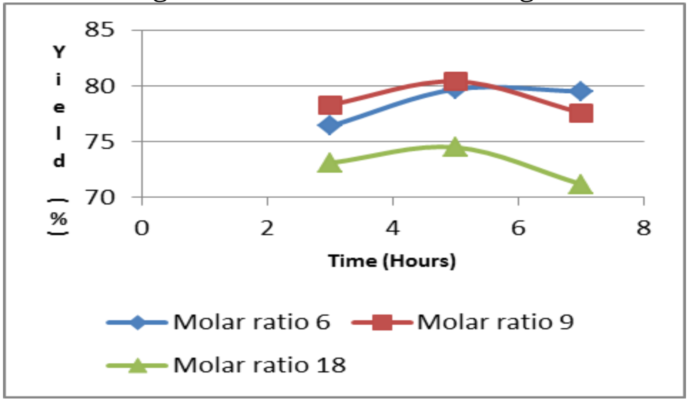


Figure 4.2: Results for 5% weight

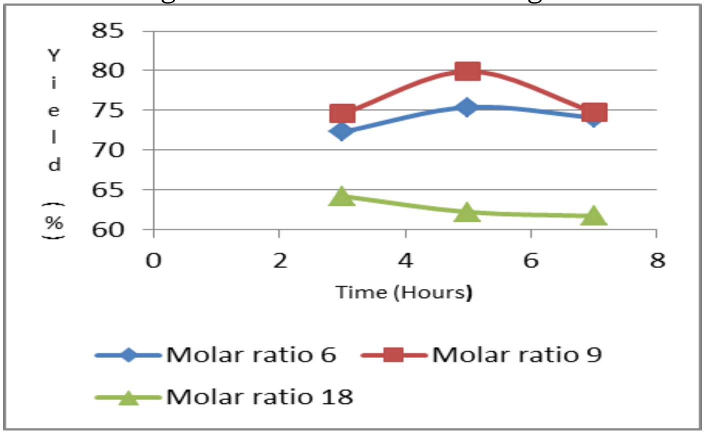


Figure 4.3 Results for 7% weight

4.2 Optimization of Catalyst Weight %:

The reactions were conducted with catalyst weight percentages of 3%, 5% and 7%. Of the three the maximum yield was obtained at 3% weight. To obtain the optimal value, numerical search method was used. Since the yield was lower at 5% than 3%, the next trials were conducted at 2 and 4%. The maximum yield of 83.36% was obtained at 4% weight of catalyst and hence 4 % catalyst weight was concluded as the optimal value. The results of catalyst weight % vs. yield % are shown in figure 4.4.

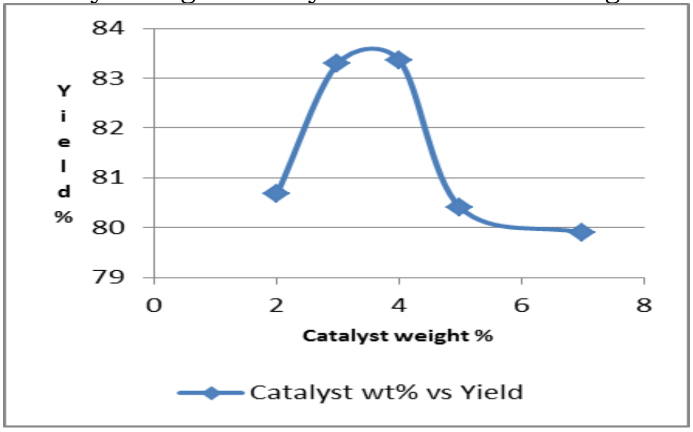


Figure 4.4: Catalyst weight % vs. yield

4.3 Optimization of Potassium Loading:

All the above experiments were conducted with 10 % potassium loading on the catalyst. To optimize the percentage loading of potassium, search method was used. From the above cases it was concluded that the most optimal parameters are 4% catalyst weight, methanol: oil molar ratio 9, reaction time 5 hours. Now with these optimized conditions, experiments were carried out with various potassium loadings, such as 2%, 5%, 7% and 12%. The results obtained are shown in figure 4.5. it can be seen that a maximum yield of 83.36% was obtained at 7% potassium loading.

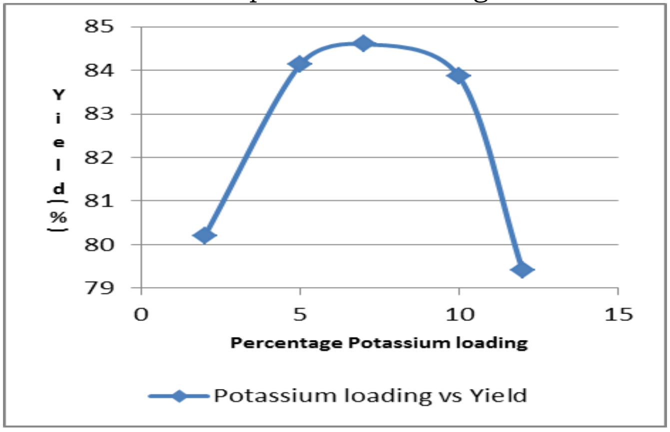


Figure 4.5: Potassium loading % vs. yield

5. Conclusion:

The present study explore the variation in yield of biodiesel using potassium loaded TiO$_2$. A maximum yield of 83.36% was obtained at 4% catalyst weight, methanol to oil molar ratio of 9, reaction time of 5 hours and potassium loading of 7%. The catalyst was characterized using XRD and HRTEM techniques and was found to have an average size of 200nm. The effect of the catalyst after optimization was that it resulted in 7% higher biodiesel yield compared to the base catalyst KOH. The catalyst promises to be potential candidate for large scale biodiesel production at reduced cost and energy usage.

6. References:

1. Rajesh Madhuvilakku, Shakkthivel Piraman.2013 ",Biodiesel synthesis by TiO2–ZnO mixed oxide nanocatalyst catalyzed palm oil transesterification process " Bio resource technology 150, PP. 55-59.
2. Yun hin taufiq-yap, Nurul fitriyah Abdullah Mahiran basri,2011, " Biodiesel Production via Transesterification of Palm Oil Using NaOH/Al2O3 Catalysts" Sains Malaysiana 40(6)(2011): PP587–594
3. Venkata Ramesh Mamilla, M. V. Mallikarjun, Dr.G.Lakshmi Narayana Rao 2008." Preparation of Biodiesel from Karanja Oil", International Journal of Energy Engineering Vol.1 No.2 2011 PP.94-100.
4. Mookan Rengasamy, Sundaresan Mohanraj, Senthilkumar Harsha Vardhan, Ravichandran Balaji, Velan Pugalenthi. "Transesterification of castor oil using nano-sized iron catalyst for the production of biodiesel", National Conference on plant Metabolomics 2014 ; PP 108-112
5. H. I. El-Shimi, Nahed K. Attia, S. T. El-Sheltawy, G. I. El-Diwani, Biodiesel Production from Spirulina-Platensis Microalgae by In-Situ Transesterification Process Journal of Sustainable Bioenergy Systems, 2013, 3,PP 224-233.
6. Daniela Salinas, Sichem Guerrero , Paulo Araya Transesterification of canola oil on potassium-supported TiO2 catalysts Catalysis Communications 11 (2010) PP 773–777
7. Vishal Mutreja,a Satnam Singh,Tajbir Kaur Minhasb Amjad Alib "Nanocrystalline potassium impregnated SiO2 as heterogeneous catalysts for the transesterification of karanja and jatropha oil" An international journal to further the chemical sciences 2015, PP 46890-46896 .
8. Canakci, M., 2007. The potential of restaurant waste lipids as biodiesel feedstocks. Bioresour. Technol. 98, 183–190.
9. Chen, Y.H., Chen, J.H., Chang, C.Y., Chang, C.C., 2010. Biodiesel production from tung (Vernicia montana) oil and its blending properties in different fatty acid compositions. Bioresour. Technol. 101, 9521–9526.
10. Hu, S., Wen, L., Wang, Y., Zhen, X., Han, H., 2012. Gas–liquid countercurrent integration process for continuous biodiesel production using a microporous solid base KF/CaO as catalyst. Bioresour. Technol. 123, 413–41