

Chapter 6

Valorization of Waste Date Seeds for Green Carbon Catalysts and Biodiesel Synthesis



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Abstract The decreasing availability of fossil fuels and environmental issues associated with their use has placed a greater emphasis on biofuels production as a competent alternative source to produce energy in the current era. Production of biofuels from plant-based oil has a good prospect as a competent alternative to fossil fuels. The concept of utilizing waste date pits for biofuels production is promising due to its abundant availability in Oman. Present work reports, a better way to

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valorize the waste biomass (Date pits) is adopted in order to get environment friendly catalyst which will be effectively used for producing biodiesel. The produced carbon material was impregnated with KOH to enhance the efficiency and analyzed by SEM, XRD, EDX and BET. The production of biodiesel was analyzed by parametric studies involving following process parameters which include process temperature, reaction time, type of catalysts along with methanol to oil ratio. The maximum yield obtained was 91.6% for following parametric value such as temperature 65 °C, for C3 (6 wt% KOH on carbon) catalyst when 9:1 methanol to oil ratio was used. Moreover, the verification for quality of produced biodiesel was done by comparison with standards recognized internationally (ASTM and EN). The produced biodiesel possessed a cetane number of 60.31, density 881 kg/m³, flash point 141 °C, viscosity was measured to be 4.24 mm²/s, low temperature properties which includes cloud point, cold filter plugging point and pour point were 3.9 °C, −0.62 °C, −1.4 °C respectively thus these properties identify the quality of produced biodiesel. Thus, all properties were within the ranges provided standards of ASTM and EN. Thus, it can be concluded that Date pits biomass is potential alternative source for catalyst synthesis along with biodiesel.

Keywords Waste biomass, carbon catalyst · Biodiesel · Energy source

6.1 Introduction

Currently, fossil fuels are sources for energy production and only source for energy supply (Bae and Kim 2017; Abas et al. 2015; Mohr et al. 2015). As in the last century world observed the industrial revolution, this enhanced the economic activity which lead to increase the energy demand and utilization (Vertes et al. 2010), carbonaceous fuel which are fossil-based emerged as a main source for production of energy and in transportation (Fig. 6.1) (Shafiee and Topal 2009). In 2014, oil consumption was approximately 92 million barrels per day worldwide (2015) and is expected to reach 116 million barrels per day in 2030 (Cherubini 2010). This hasty upsurge in oil usage has led to questions regarding its readiness and issues related to environmental caused by combusting fossil fuels.

As shown in Fig. 6.2, the depletion of fossil oil reserves is due to rapid industrial growth and population growth which caused the increase in demand for fossil fuel. 42% of the world's energy is produced by consuming fossil oil indicating the importance of fossil fuel as the major source for economic development. According to the 2016 report of the Energy Information Administration (EIA) report, it is estimated that the world's total energy consumption will increase by 71% between 2000 and 2030 based on population increment and welfare. The usage of oil, coal and gas will increase by 30–50% of current value and 75% of energy produced will be from coal, gas and oil in 2040 (Grammelis et al. 2016; Di Gianfrancesco 2017). Oil production may its maximum in 2030. Meanwhile, conventional fossil oil is

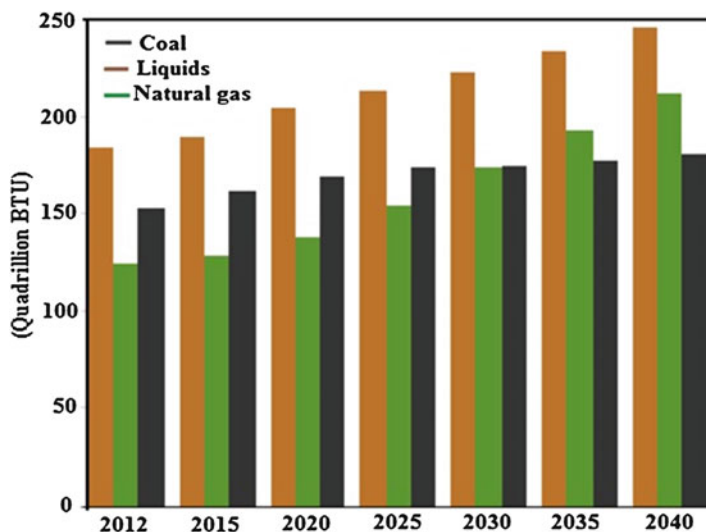


Fig. 6.1 Worldwide fossil fuel energy consumption from 2012 to 2040 (EIA 2012)

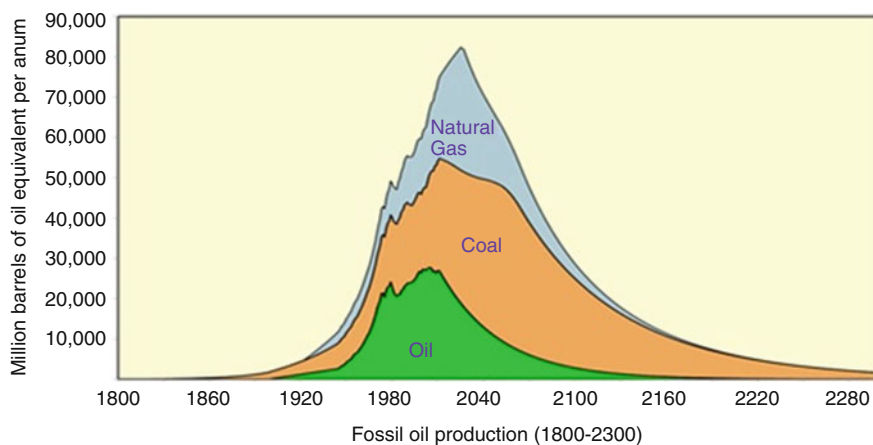


Fig. 6.2 Fossil reserves exploration and usage worldwide and their consumption (Archibald 2014)

expected to be constrained by reduced supply owing to physical depletion and decreased accessibility to oil possessing area (Capellán-Pérez et al. 2014; Utama et al. 2014). Due to depletion of fossil fuel reserves the transportation sector may be affected to a large extent as it consumes more than 50% of oil being produced worldwide (Dewulf et al. 2005; Vertes et al. 2010; Panwar et al. 2011). Similarly, the chemical industry is expected to be second most affected sector due to a decreased supply of fossil oil. The demand for fuel increases ostensibly due to increasing need for fertilizers, plastics, electricity and chemicals which puts pressure on the available energy supply and infrastructure.

Based on the trend followed by oil consumption, it can be concluded that fossil oil supply will not be able to meet demand in the coming era. Therefore, environmental and availability concerns related to the usage of fossil-based fuels can be overcome by utilizing alternative energy sources. Hence, renewable and sustainable resources such as wind, biomass and solar energy can counterpoise the concerns related to fossil fuels (Tiwari and Mishra 2011). Moreover, among all alternative energy resources mentioned, biomass is the most suitable alternative based on the fact that it is an enriched source of carbon. Also, it can serve as a source of energy as well as biochemicals and catalysts. In spite of this solar and wind can only serve as a source of energy (Demirbas 2007; Maczulak 2009).

6.2 Biomass as an Alternative Source

Biomass is the material resulting from resources naturally present in the environment or biological matter derived from living organisms (Klass 2006; Vertes et al. 2010). It possesses a complex chemical nature and its composition relies on factors such as location and environment of its growth. Biomass is regarded as renewable as its production is the result of photosynthesis as a result of energy captured from sunlight, which leads to the growth of plants (Ptasinski 2016; Ringsmuth et al. 2016). Meanwhile, when biomass itself or its derived products are combusted, CO_2 is released into the environment where it may be recaptured as seen in Fig. 6.3, which shows the complete carbon cycle (Rosillo-Calle and Woods 2012). It is thought to be the best potential alternative to fossil-based fuels based on its sustainability and reliability as a competent source of organic compounds, which can be utilized as green fuels, chemicals and materials. Thus, moving towards the

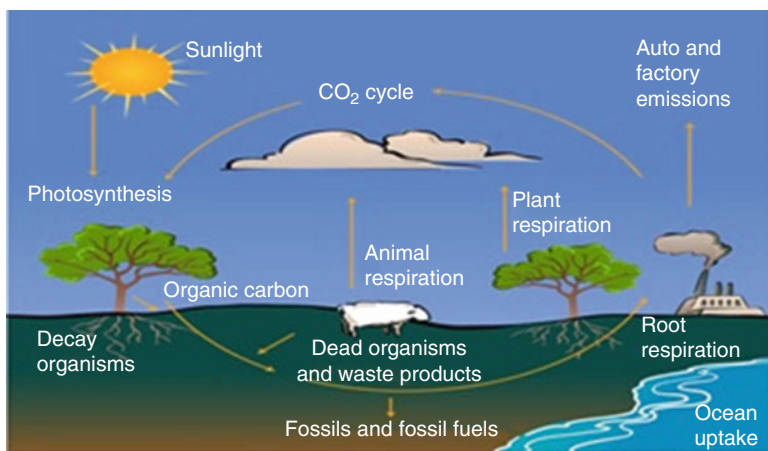


Fig. 6.3 Carbon cycle for all kinds of emissions and use of CO_2 for photosynthesis (Carbon-Cycle 2018)

sustainable energy sources causes the urgent need for the valorization of biomass. Therefore, bringing biomass-derived fuels, chemicals and materials to the commercial level requires the development of efficient technologies and this leads this to be one of the main research domain of current era.

Sustainability and environmental related issues regarding biomass usage have been considered in terms of industrial-scale production of biofuels based on the first generation biofuels. First generation biofuels were derived from edible feedstocks which may lead to food versus fuel controversy and reduce biodiversity (Vertes et al. 2010). Thus, this is considered to be the major drawback for the biofuels production that may increase the edible oil prices and causes food scarcity in a specific area of biofuel production and it can be overcome by using non-edible feedstocks.

The sustainability of biomass depends on its source type and it should be abundantly available for producing biofuels and chemicals. One can prove the sustainability of biomass based on some parameters such as growth on abandoned agricultural land, crop waste, harvested plants from forests and organic waste generated from industrial and domestic purposes (Tiwari and Mishra 2011; Toka et al. 2014). Moreover, biomass used for biofuels production should have high energy density. Biomass processed auxiliaries and produced fuels along with waste are considered to biodegrade either by bacteria or other biological means more rapidly as compared to fossil-derived products and waste (Ptasinski 2016).

6.3 Feedstock Selection

Almost 90% of biofuels are being produced from edible oils due to a global imbalance in the market demand and food supply by their high prices and the reduction of food sources it should be shifted towards non-edible oils sources (Mofijur et al. 2013). Due to the presence of some toxic components in non-edible oils such as protein curcin and purgative in jatropha plants, castor plant contains protein ricin, glucoside cerberin in fruits of sea mango and flavonoids pongamiin and karajiin in karanja oil, they are not considered good for health (Banković-Ilić et al. 2012). Non-edible oil-producing plants are grown all over the world but of different types. Also, while considering the plantation of non-edible plants, they can be grown over barren lands not suitable for cultivation and moreover, help to reduce CO₂ as well from the environment. Worldwide production of different kinds of feedstocks is shown in Table 6.1. In addition, biofuels produced from non-edible resources can become a major poverty alleviation program for rural areas by providing them with energy security and upgrading the non-farm rural sector (Jamil et al. 2018). Finally, all these factors lead to the feasibility of considering the sustainability of biofuels production.

There are some issues also related to the non-edible oils for biofuels production such as they have a high acid value which refers to high contents of free fatty acids, high viscosity and high oxygen contents which can affect the engine performance during their combustion (Yusuf et al. 2011). However, it must be pointed out that

Table 6.1 Different kind feedstocks available in different regions

Country	Feedstock
USA	Waste oil/soybeans/peanut
Canada	Rapeseed/animal fat/soybean/yellow grease
Mexico	Waste oil/animal fat
Germany	Rapeseed
Italy	Rapeseed/sunflower
France	Rapeseed/sunflower
Spain	Lin seed/sunflower
Greece	Cotton seed
UK	Waste cooking oil/rapeseed
Sweden	Frying oil/animal fat
Ireland	Rapeseed
India	Jatropha/rapeseed/sunflower
Malaysia	Palm oil
Indonesia	Palm oil/jatropha/coconut
Singapore	Palm oil
Philippines	Coconut/jatropha
Thailand	Palm oil/jatropha/coconut
China	Waste cooking oil/rapeseed/jatropha
Brazil	Soybeans/palm oil/castor/cotton oil
Argentina	Soybeans
Japan	Waste cooking oil
New Zealand	Waste cooking oil/tallow
GCC	Date palm

global biofuel feedstocks should not rely on certain sources as it could bring harmful influence in the long run. The world's dependence on the fossil fuels is the perfect example. Therefore, biofuels feedstock should be as diversified as possible, depending on their geographical locations in the world.

6.4 Biomass Availability

Date palm is considered the main crop in Oman which occupies 54 percent of total agricultural land in the country (El Hag et al. 2002, 2014). Date palm exists in large amounts in Oman with around 200 cultivated varieties and a production rate of about 270,000 metric tons per year from an area of 31,500 hectares. The total production of dates in Oman reached 308,000 tonnes in 2013 from 281,000 tonnes in the previous year, according to the latest data released by the Ministry of Agricultural and Fisheries (2014). The ministry had conducted a detailed survey of the most important crop of the country during 2013. It revealed that out of the 308,000 tonnes, only 7000 tonnes were exported. According to the statistics, the local consumption within the country was 164,000 tonnes when the population of the country was 2,159,000

(2014). On average, a single person consumed 60 kg of dates annually. This is in addition to 1,710,000 expatriates, who, on average consumed around 20 kg of dates per person. Oman ranks ninth in the world dates production, however, its export share is only around 4% of all dates produced (Manickavasagan et al. 2012). Majority of dates are used for human consumption (51%), while animal consumption constitutes 22%. This would deliver around 62,000 metric tons of residues that represent 23% of the total date production.

6.4.1 Potential of Utilizing Waste Date Pits for Biofuel Production

Based on Date palm production it can be reported that Oman can potential candidate for supplying biomass waste for biofuel production. Date palm waste (pits) has outstanding potential as an substitute energy supply as it evades the use of the edible parts of the plant, hence does not compete with the food supplies for biodiesel synthesis. The by-product from dates is date pits. They are largely available in Oman and are usually very cheap. They can, therefore, be used as a source for producing biofuel. The residues of date palm tree and spoiled dates comprise economic and environmental burden to be managed. Interestingly, date pits contain 15–20% volatile compounds that can be a potential source for biofuel production. There are two main pathways used to obtain oil such as fermentation for bioethanol production and oil extraction and transformation of that oil to biofuel. The fermentation process could be time-consuming while the yield is low. For these reasons, obtaining biofuel from oil extracted from date pits is a preferred method and so the biofuel production from date pits would be a very attractive option. Amani et al. (Amani et al. 2013) produced biodiesel from the oil extracted from date pits by transesterification and reported that the biodiesel produced fulfilled international standards for biodiesel. Azeem et al. (2016) studied the potential of various varieties of date pits for biodiesel production. They found that biodiesel from waste date pits possesses the fuel properties which meet the international standards. Biofuel production from renewable resources in Oman such as date pits will not only help in recycling the vast amount of waste materials produced in the country but will also provide the local and governmental authorities with the economic and technical benefits of biofuel. The use of biofuel may replenish any future shortage of fossil fuels due to continuous population growth and will decrease the greenhouse gas emission.

6.4.2 Waste Date Pits

Date pits (*Phoenix Dactylifera L.*), were collected from a local “Dates” farm in Muscat. The pits were brown in visual appearance as shown in Fig. 6.4. As pits were



Fig. 6.4 Waste date pits (a) original form, (b) powder of waste date pits and (c) grinder used for grinding

collected from the farm, they were treated as waste. So, first of all, they were cleaned and then washed with water in order to remove dirt and pulp. The pits (15–20 wt% moisture content) were then sun-dried for 6–7 days, followed by overnight drying in an oven at 70 °C to completely remove the moisture content from date pits. The dried pits were rigid and hard. Hence, the strong mechanical grinder was used to grind them into powder form. The powdered material obtained after grinding was sealed so as to avoid moisture contamination and open just before use. The grinder used for grinding the waste date pits is shown in Fig. 6.4c. Ground date pits were used to extract the oil in a Soxhlet apparatus in which hexane was used as a solvent. Standard method AOCS was adopted for extraction.

6.5 Biodiesel

The term biodiesel refers to the alkyl esters of plant oils and animal fats produced by transesterification (Bart et al. 2010a, b, Knothe 2010). Biodiesel ought to be a combination of saturated and unsaturated fatty acids and monoalkyl esters derived from edible and non-edible sources. It is considered as an alternative fuel to conventional diesel if it complies with international standards (American Society of Testing and Materials ASTM D6751 and European standard EN 14214) (Bart et al. 2010a, b; Chen et al. 2013, Aransiola et al. 2014, Baroi and Dalai 2015). The increasing trend of adopting the biodiesel as a competent alternative to fossil diesel is due to its physiochemical properties and energy content which allows it to be used directly or in blended form with conventional diesel in compressed-ignition engines without modification (Gerhard et al. 1997).

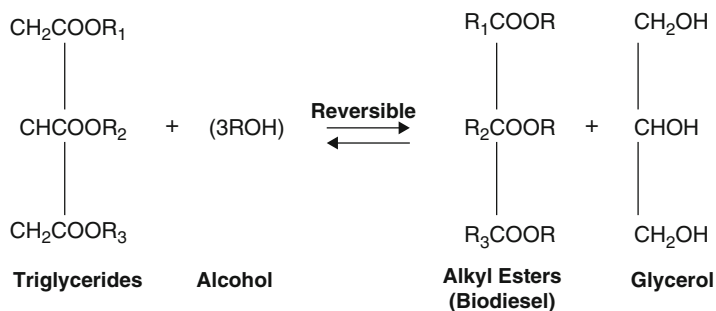


Fig. 6.5 Transesterification of triglyceride to form alkyl ester and glycerol as a by-product (Demirbas 2008)

Transesterification refers to the reaction in which triglycerides react with alcohol in the presence of suitable catalysts and give monoalkyl ester (Demirbas 2007; Demirbas 2008) as shown in Fig. 6.5. This is also known as alcoholysis and considered to be most suitable technique compared to others used for upgrading plant-based oils and animal fats to consumable fuel for energy production or transportation purposes (Jitputti et al. 2006; Meher et al. 2006). The product fuel obtained from this process is known as biodiesel and is one of the most commonly used and commercialized products from plant-based oils and animal fats. Transesterification is not a new method; it was first reported in 1853 in which alcoholysis of castor oil was done with ethanol, but the desired product was glycerol (Demirbas 2005). It is considered to be cheapest among other techniques used for upgrading plant-based oils and animal fats and to overcome the major problem of the higher viscosity of oils (Yan et al. 2007; Liang et al. 2009a, b). The important factors, which one should consider before applying transesterification for upgrading oils are fatty acid content, the water content in oil, amount of saturated component in fatty acids and components which cannot be converted such as sterols, hydrocarbons and tocopherols. The water content of oil should be less than 0.5% because it leads to hydrolysis of oil to generate FFAs, which cause soap formation in the presence of alkaline catalysts (Chouhan and Sarma 2011; Lin et al. 2011). The amount of saturated components does not affect the process as such but it can lead to poor properties of biodiesel produced. Meanwhile, the percentages of non-convertible should not exceed 1.5%. If they are more than that, this indicates that there is some contamination in oil and it should be filtered before transesterification (Mofijur et al. 2013).

6.5.1 Biomass Collection and Catalysts Synthesis

Date pits were gathered from nearby food processing factory located in Muscat, Oman. Firstly the date pits were grinded and powdered material was washed in order

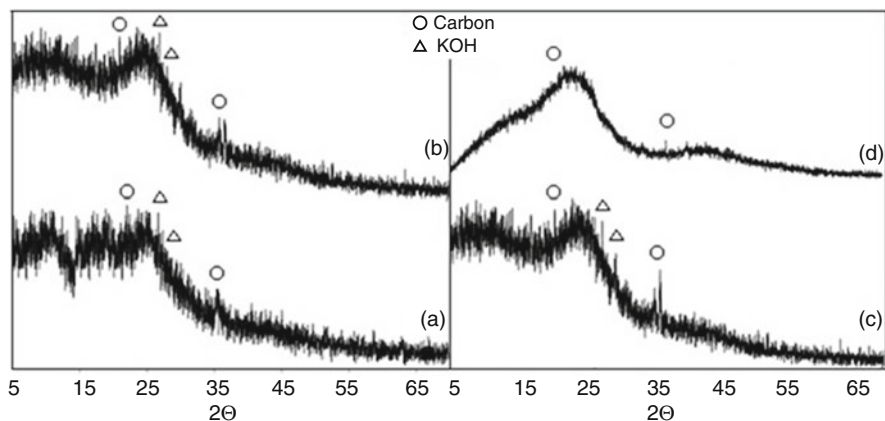


Fig. 6.6 XRD results: (a) catalysts C1; (b) catalysts C2; (c) catalysts C3 and (d) pristine carbon (Abu-Jrai et al. 2017)

to remove all impurities. The washed material was placed in oven for 6 h at 110 °C so as to remove moisture from powdered biomass. After drying the material was carbonized in muffle furnace at 500 °C in absence of oxygen for 4 h and heating rate applied was 3.5 °C/min. Further on the carbonized material was further washed to remove all kind of impurities and obtained pristine carbon. The pristine carbon was dried in oven for four hours at 110 °C. The pristine carbon was further modified by impregnating with KOH solution in different amounts (2 wt%, 4 wt% and 6 wt %). Pristine carbon was mixed with aqueous solution of KOH for almost 24 h at atmospheric conditions so as to impregnate KOH in carbon. The pristine carbon material modified with KOH in several ratios was first filtered and then dried. The produced catalysts were denoted as C1 (2 wt% KOH with carbon), C2 (4 wt% KOH with carbon) and C3 (6 wt% KOH with carbon).

X-ray powder diffraction (XRD) patterns were measured on PANalytical (Xpert PRO instrument, USA) fitted out with revolving anode and $\text{CuK}\alpha$ radiations. The analysis were carried out in continuous $\theta/2\theta$ scan refraction mode for synthesized catalysts. The results of XRD for pristine carbon along with modified carbon with KOH are given in Fig. 6.6. Two prominent peaks are seen in pattern for pristine carbon such as 21°–24° and 35°–43° which relates to pure carbon and graphite respectively. Thus there were several peaks present in patterns given for modified form of catalysts which can be related due to impregnation of KOH. The peaks which ranges between 26°–35° can be due to KOH in modified forms of pristine carbon derived from waste Date pits biomass. Thus it can be concluded based on patterns given by XRD that KOH has been successfully impregnated in pristine carbon.

Scanning Electron Microscope (SEM) was used to measure crystal and surface morphology in SEM (JEOL JSM-7900F instrument, Japan). Images shown in Fig. 6.7 are for pristine carbon along with its modified forms. It was observed from images that there was not any margin change between images. Moreover the

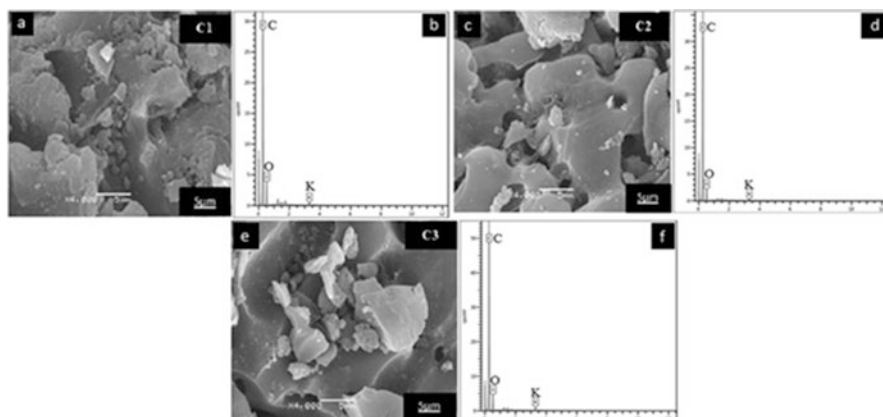


Fig. 6.7 SEM images for (a) pristine carbon with 2 wt% of KOH (C1); (b) EDS of C1; (c) carbon with 4 wt% of KOH; (d) EDS of C2; (e) carbon with 6 wt% of KOH and (f) EDS of C3. (Abu-Jrai et al. 2017)

Table 6.2 BET results for pristine carbon along with its modified forms

Sample ID	S_{BET} (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
C	432.1	0.22	6.62
C ₁	229.5	0.17	6.41
C ₂	218.2	0.15	6.19
C ₃	210.5	0.14	5.98

images shows that there are not agglomerates present which lead to observation that KOH is dispersed uniformly on the waste date pits carbon and small changes in the images as shown in Fig. 6.7a, b and c might be due to increment in the concentration of KOH. Further EDX results gave assurance of well distribution of KOH on parent carbon material.

The catalysts were further analyzed through BET analyzer (ASAP 2020, Micromeritics Instruments Inc., Norcross, GA, USA) using nitrogen gas (99.995% pure) to determine surface properties such as surface area, size of pores and volume of pores as carbon material is highly porous. The measurements done in BET are shown in Table 6.2. It was observed that significant decrement in surface area and pore volume in modified form of pristine carbon which can be attributed to the fact that KOH articles occupied the pores up to some extent which affect the activity of catalysts. However, the final shows that pore size is up to marks so that it can support trans esterification.

So, it can be concluded based on all characterization that efficient catalysts have been synthesized with uniform distribution of KOH on parent carbon material. Moreover, it can stated that as amount of KOH is being increased tends to enhance the active site for trans esterification to produce biodiesel. Pore channel is basic requirement for biodiesel formation based on BET results it can be concluded that

synthesized catalysts have definite pore channel along with active sites. As shown that all catalysts possess pore diameter even higher than the diameter of triglyceride molecule 5.8 nm (Wan Omar and Amin 2011). Thus it can be concluded that C3 can be more active attributed from the fact that it can provide more basic sites and suitable pore channel.

6.5.2 Biodiesel Production

Oil was extracted using a paper thimble (43 mm, Whatman International Ltd., Maidstone England), Firstly the powder biomass was placed in thimble and cotton was used to cover it from top and placed in Soxhlet assembly for oil extraction. Extraction process was done for 7 h while using n-hexane as solvent and once extraction time is over the mixture of oil and solvent are separated by using rotary evaporator (Buchi, Switzerland). To produce transesterification was carried out in two neck flask and experiments were done according to plan developed by using RSM software using Taguchi's method as mentioned in Table 6.3. Parameters under consideration were temperature, methanol-to-oil ratio, time, and catalysts type against the yield of biodiesel which set as response factor calculated experimentally based on Eq. 6.1.

$$Yield = \frac{wt\ of\ methyl\ produced}{wt\ of\ oil\ as\ feed} \times 100 \quad (6.1)$$

6.5.3 ANOVA Analysis

Significance of all process variables was determined through statistical analysis known to be ANOVA. First of all a model is predicted based on experimental data

Table 6.3 Plan for experiment developed using RSM

Time (min)	Temperature (°C)	Catalyst type	Alcohol: Oil	Yield (%)
80	65	1	15	82.1
80	60	3	12	70.1
40	70	3	15	77.4
80	70	2	9	83.7
60	65	3	9	91.6
60	70	1	12	84.8
40	60	1	9	75.3
60	60	2	15	73.1
40	65	2	12	82.9

Table 6.4 ANOVA analysis for transesterification of date pits oil

Source	F-value	p-value Prob > F
Model	65.97	0.015
Time (min)	23.32	0.041
Temperature (°C)	142.8	0.007
Alcohol: Oil	31.74	0.033
ANOVA analysis		
Standard deviation	0.95	
Corrected value (%)	1.18	
R-squared	0.995	
Signal/noise	25.682	

obtained by RSM and p-value test predicts which model is most suitable for current process. For p-value test the value should be less than 0.05 then it is significant with more than 95% confidence level. Further on coefficient of determination (R^2) gave another prediction for most significant model for current process and its variance from experimental data. In order to examine the current process ANOVA analysis is performed and shown in Table 6.4.

As discussed earlier that for significant model p-value should be less than 0.05 thus for current process model p-value is 0.015 which gave the understanding that model is significant with more than 95% level of confidence. In similar value this p-value also indicates the significance for each parameter along with interaction parameter and cross products. Thus, ANOVA study told that how nominal affect is of parameters on yield of biodiesel and based on results it can be revealed that the most significant effect was of temperature on yield of biodiesel. The predicted model is shown in Eq. 6.2.

$$\text{Yield} = 80.11 - 1.58A[1] + 3.06A[2] - 7.28B[1] + 5.42B[2] + 3.42D[1] - 0.84D[2] \quad (6.2)$$

High level of accuracy is obtained when CV is low which is the actual indicator for good agreement between experimentally determined values of biodiesel yield and values taken based on model predicted from ANOVA analysis. Moreover this was further justified by high value near to 1 of R^2 which gave good fitting of experimental value with model predicted value. Thus this can be also observed from the plot shown in Fig. 6.8 as actual yield and predicted yield has good coincidence between each as they are almost linear with each other. Similarly, it can be seen in Fig. 6.8 that response values calculated based on the predicted and actual experimental value were in good agreement.

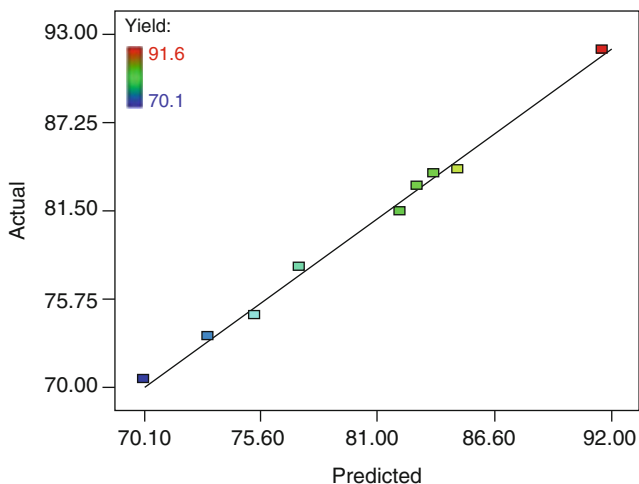


Fig. 6.8 Biodiesel yield actual vs predicted values (Abu-Jrai et al. 2017)

6.5.4 Parametric Study

In order to examine the effect of process parameters on biodiesel yield a detailed parametric is conducted as shown in Fig. 6.9. First of all process time was considered and other parameters were constant. It can be observed from figure that as the time is increased biodiesel yield start increasing but this behavior was upto certain time and after that the decreasing trend was observed. Thus trend the of time can be attributed to fact that initially time was not enough for reactants to interact and form the product. Moreover as time start increasing the yield increased lead to observation that reactants got enough time to interact and form the product but the decrement in yield may be attributed to the observation that due to difficulty in separation of downstream process while the reaction is reversible thus cause the decrement in yield of biodiesel. Process temperature is one of the important parameter to be analyzed and as shown in figure it can be observed that initially at low temperature biodiesel yield was quite low. However with the increment in temperature a significant increase in yield was observed. Similarly to time temperature also gave similar kind of trend. The yield increased up to certain limit and after that the yield decreased by increasing temperature. This observation can be related to the fact that but increasing the temperature the affinity of reactants increases and they react to form biodiesel. However, as the temperature is increased further the availability of methanol in reaction vessel starts decreasing thus causing the reversible reaction and tending to decrease the biodiesel yield. (Gurunathan and Ravi 2015). Another parameter studied was methanol to oil ratio and its effect on biodiesel is shown by Fig. 6.9c. As the reaction is reversible based on this fact excess methanol is provided so as move reaction into forward direction and according to stoichiometric calculation, molar ratio of methanol to oil 3:1 is required only for transesterification

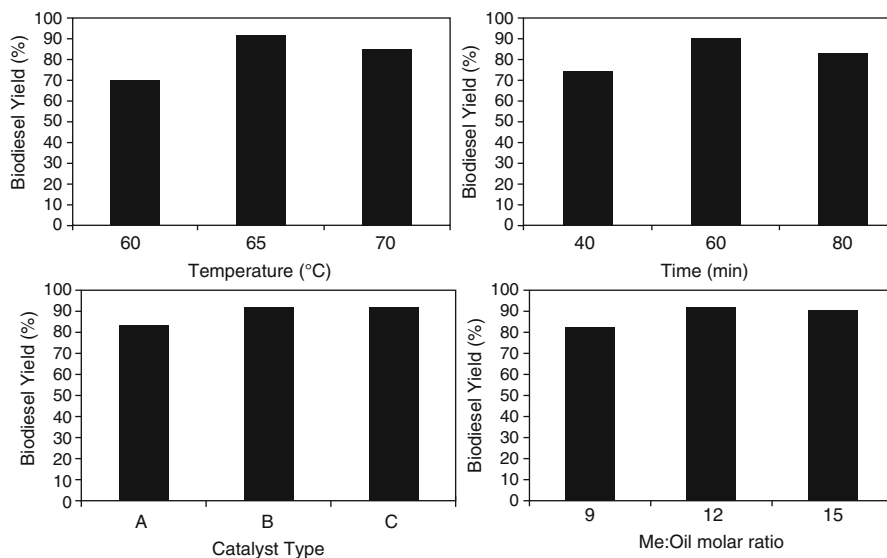


Fig. 6.9 Biodiesel yield with respect to temperature, time, catalyst type and methanol to oil ratio

reaction. Based on the trend shown in the figure it can be said that by increasing ratio tend to increasing the yield of biodiesel but increasing the ration further yield of biodiesel decreased tending to the observation that higher ratio may obstruct the separation of byproducts and leading to decrement in biodiesel yield. In the last effect a catalyst loading was studied and tend in shown in Fig. 6.9d. It can be observed that both catalyst C1 and C2 gave lower yield of biodiesel as compared to C3. This can be related to the fact that in C3 there was more quantity of KOH and thus this tends to provide more active sites for the reaction. Based on the parametric study conducted it can be suggested that optimum conditions are 65 °C process temperature, for 1 h reaction time when C3 catalysts was used with methanol to oil ratio 9:1 and biodiesel yield was 91.6%.

6.5.5 Quality of Biodiesel

Quality of any fuel synthesized is to be determined before claiming its suitability to be used as fuel. Thus several techniques given by international standards ASTM and EN were considered for evaluation of produced biodiesel. It was observed that biodiesel produced gave cetane number 60.31 that fulfill the minimum requirement defined by standards. One of major drawback of biodiesel to be used as a fuel is its bad low temperature properties in colder regions. But the produced biodiesel gave better low temperature properties which were cloud point 3.7 °C, pour point is -1.6 °C and cold filter plugging point -0.62 °C. Thus for *Phoenix dactylifera*

kernel oil, low-temperature properties are quite considerable. Moreover, other measured properties include flash point and calorific values which were 141 °C and 43.24 MJ/kg respectively. As flash point refers to the temperature above which fuel may ignite thus for produced biodiesel flash point is higher than the minimum limit defined by standards. Further on kinematic viscosity and density of produced biodiesel was observed to be at 40 °C was 4.24 mm²/s and 881 kg/m³, respectively. One of major property which can help to establish the observation that either fuel storage is safe or not in terms of corrosion is acid value and for produced biodiesel is 0.32 mg KOH/g and this less than the limit defined by ASTM and EN standards thus enables its storage and transportation safe.

6.6 Conclusions

All parts of the world are facing issues regarding the depletion of fossil reserves due to excess usage and ever-increasing demand. Moreover, combustion of fossil fuels causes environmental pollution due to emission of excess CO₂, thus all these issues lead the search for an alternative source for energy production and transportation sector. Biomass is considered to be a promising alternative for reducing demand and consumption of fossil-based fuel reserves. In Oman, abundantly available biomass from agricultural waste is date pits which are valorized in present research work to biofuels and catalysts. First of all, grinded date pits were used to extract the oil in Soxhlet apparatus in which hexane was used as solvent. Standard method AOCS was adopted for extraction.

Date palm waste (pits) were effectively engaged for oil extraction and carbon post oil extraction was engaged in catalysts synthesis successfully to produce biodiesel. Moreover, it was revealed based on characterization that impregnated material was uniformly distributed and gave equal number of active sites for biodiesel production. Based on the parametric study conducted it can be suggested that optimum conditions are 65 °C process temperature, for 1 h reaction time when C3 catalysts was used with methanol to oil ratio 9:1 and biodiesel yield was 91.6%. Moreover produced biodiesel was suitable for commercial usage as fuel based on fuel properties measurement and their comparison with standards ASTM and EN.

So, the conclusive remark for overall research work reported was to valorize waste date pits which are abundantly available in Oman. All aspects were considered, such that the oil extracted was subjected to the production of biofuel such as biodiesel. Moreover, biodiesel was produced in the presence of heterogeneous carbon catalysts which help to overcome issues related to usage of conventional homogeneous catalysts. The synthesized catalyst was highly active which makes biodiesel production economical.

References

- Abas N, Kalair A, Khan N (2015) Review of fossil fuels and future energy technologies. *Futures* 69 (0):31–49. <https://doi.org/10.1016/j.futures.2015.03.003>
- Abu-Jrai AM, Jamil F, Al-Muhtaseb A a H, Baawain M, Al-Haj L, Al-Hinai M, Al-Abri M, Rafiq S (2017) Valorization of waste date pits biomass for biodiesel production in presence of green carbon catalyst. *Energy Convers Manag* 135:236–243. <https://doi.org/10.1016/j.enconman.2016.12.083>
- Amani MA, Davoudi MS, Tahvildari K, Nabavi SM, Davoudi MS (2013) Biodiesel production from Phoenix dactylifera as a new feedstock. *Ind Crop Prod* 43(0):40–43. <https://doi.org/10.1016/j.indcrop.2012.06.024>
- Aransiola EF, Ojumu TV, Oyekola OO, Madzimbamuto TF, Ikhu-Omoregbe DIO (2014) A review of current technology for biodiesel production: state of the art. *Biomass Bioenergy* 61 (0):276–297. <https://doi.org/10.1016/j.biombioe.2013.11.014>
- Archibald D (2014) The Twilight of Energy Abundance. SPE Asia Pacific Oil & Gas Conference and Exhibition. Adelaide, Australia, Society of Petroleum Engineers
- Azeem MW, Hanif MA, Al-Sabahi JN, Khan AA, Naz S, Ijaz A (2016) Production of biodiesel from low priced, renewable and abundant date seed oil. *Renew Energy* 86:124–132. <https://doi.org/10.1016/j.renene.2015.08.006>
- Bae C, Kim J (2017) Alternative fuels for internal combustion engines. *Proc Combust Inst*. <https://doi.org/10.1016/j.proci.2016.09.009>
- Banković-Ilić IB, Stamenković OS, Veljković VB (2012) Biodiesel production from non-edible plant oils. *Renew Sust Energ Rev* 16(6):3621–3647. <https://doi.org/10.1016/j.rser.2012.03.002>
- Baroi C, Dalai AK (2015) Process sustainability of biodiesel production process from green seed canola oil using homogeneous and heterogeneous acid catalysts. *Fuel Process Technol* 133:105–119. <https://doi.org/10.1016/j.fuproc.2015.01.004>
- Bart JCI, Palmeri N, Cavallaro S (2010a) 1 – Biodiesel as a renewable energy source. *Biodiesel Science and Technology*, Woodhead Publishing pp 1–49
- Bart JCI, Palmeri N, Cavallaro S (2010b) 12 – Analytical methods and standards for quality assurance in biodiesel production. In: *Biodiesel science and technology*. Woodhead Publishing, Oxford, pp 514–570
- Capellán-Pérez I, Mediavilla M, de Castro C, Carpintero Ó, Miguel LJ (2014) Fossil fuel depletion and socio-economic scenarios: an integrated approach. *Energy* 77(0):641–666. <https://doi.org/10.1016/j.energy.2014.09.063>
- Carbon Cycle (2018.) <https://eo.ucar.edu/kids/green/cycles6.htm>
- Chen K-T, Wang J-X, Dai Y-M, Wang P-H, Liou C-Y, Nien C-W, Wu J-S, Chen C-C (2013) Rice husk ash as a catalyst precursor for biodiesel production. *J Taiwan Inst Chem Eng* 44 (4):622–629. <https://doi.org/10.1016/j.jtice.2013.01.006>
- Cherubini F (2010) The biorefinery concept: using biomass instead of oil for producing energy and chemicals. *Energy Convers Manag* 51(7):1412–1421. <https://doi.org/10.1016/j.enconman.2010.01.015>
- Chouhan APS, Sarma AK (2011) Modern heterogeneous catalysts for biodiesel production: a comprehensive review. *Renew Sust Energ Rev* 15(9):4378–4399. <https://doi.org/10.1016/j.rser.2011.07.112>
- Demirbas A (2005) Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Prog Energy Combust Sci* 31 (5–6):466–487. <https://doi.org/10.1016/j.pecs.2005.09.001>
- Demirbas A (2007) Progress and recent trends in biofuels. *Prog Energy Combust Sci* 33(1):1–18. <https://doi.org/10.1016/j.pecs.2006.06.001>
- Demirbas A (2008) Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. *Energy Convers Manag* 49(1):125–130. <https://doi.org/10.1016/j.enconman.2007.05.002>

- Dewulf J, Van Langenhove H, Van De Velde B (2005) Exergy-based efficiency and renewability assessment of biofuel production. *Environ Sci Technol* 39(10):3878–3882. <https://doi.org/10.1021/es048721b>
- Di Gianfrancesco A (2017) 1 – The fossil fuel power plants technology. In: *Materials for Ultra-Supercritical and Advanced Ultra-supercritical Power Plants*. Woodhead Publishing, Cambridge, MA, pp 1–49
- El Hag MG, Al-Merza MA, Al Salti B (2002) Growth in the Sultanate of Oman of small ruminants given date byproducts-urea multinutrient blocks. *Asian Australas J Anim Sci* 15(5):671–674
- Gerhard K, Robert OD, Marvin OB (1997) Biodiesel: the use of vegetable oils and their derivatives as alternative diesel fuels. *Fuels and chemicals from biomass*, vol 666. Am Chem Soc, pp 172–208
- Grammelis P, Margaritis N, Karampinis E (2016) 2 – Solid fuel types for energy generation: Coal and fossil carbon-derivative solid fuels A2 – Oakey, John. In: *Fuel Flexible Energy Generation*. Woodhead Publishing, Boston, pp 29–58
- Gurunathan B, Ravi A (2015) Process optimization and kinetics of biodiesel production from neem oil using copper doped zinc oxide heterogeneous nanocatalyst. *Bioresour Technol* 190:424–428. <https://doi.org/10.1016/j.biortech.2015.04.101>
- Jamil F, Al-Haj L, Al-Muhtaseb Ala'a H, Al-Hinai Mohab A, Baawain M, Rashid U, Ahmad Mohammad NM (2018) Current scenario of catalysts for biodiesel production: a critical review. *Rev Chem Eng* 34:267–297
- Jitputti J, Kitiyanan B, Rangsunvigit P, Bunyakiat K, Attanatho L, Jenvanitpanjakul P (2006) Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. *Chem Eng J* 116(1):61–66. <https://doi.org/10.1016/j.cej.2005.09.025>
- Klass DL (2006) *Biomass for renewable energy, fuels, and chemicals*. Academic Press An Imprint of Elsevier
- Knothe G (2010) 1 – Introduction. In: *The Biodiesel Handbook*, 2nd edn. AOCS Press, pp 1–3
- Liang X, Gao S, Wu H, Yang J (2009a) Highly efficient procedure for the synthesis of biodiesel from soybean oil. *Fuel Process Technol* 90(5):701–704. <https://doi.org/10.1016/j.fuproc.2008.12.012>
- Liang X, Gao S, Yang J, He M (2009b) Highly efficient procedure for the transesterification of vegetable oil. *Renew Energy* 34(10):2215–2217. <https://doi.org/10.1016/j.renene.2009.01.009>
- Lin L, Cunshan Z, Vittayapadung S, Xiangqian S, Mingdong D (2011) Opportunities and challenges for biodiesel fuel. *Appl Energy* 88(4):1020–1031. <https://doi.org/10.1016/j.apenergy.2010.09.029>
- Maczulak AE (2009) *Renewable energy: sources and methods (Green Technology)*, Facts on File
- Manickavasagan A, Essa MM, Sukumar E (2012) *Dates production, processing, food and medical values*. CRC Press, New York
- Meher LC, Vidya Sagar D, Naik SN (2006) Technical aspects of biodiesel production by transesterification—a review. *Renew Sust Energy Rev* 10(3):248–268. <https://doi.org/10.1016/j.rser.2004.09.002>
- Mofijur M, Masjuki HH, Kalam MA, Atabani AE, Shahabuddin M, Palash SM, Hazrat MA (2013) Effect of biodiesel from various feedstocks on combustion characteristics, engine durability and materials compatibility: a review. *Renew Sust Energy Rev* 28(0):441–455. <https://doi.org/10.1016/j.rser.2013.07.051>
- Mohr SH, Wang J, Ellem G, Ward J, Giurco D (2015) Projection of world fossil fuels by country. *Fuel* 141(0):120–135. <https://doi.org/10.1016/j.fuel.2014.10.030>
- Panwar NL, Kaushik SC, Kothari S (2011) Role of renewable energy sources in environmental protection: a review. *Renew Sust Energy Rev* 15(3):1513–1524. <https://doi.org/10.1016/j.rser.2010.11.037>
- Ptasinski KJ (2016) *Efficiency of biomass energy*. Wiley
- Ringsmuth AK, Landsberg MJ, Hankamer B (2016) Can photosynthesis enable a global transition from fossil fuels to solar fuels, to mitigate climate change and fuel-supply limitations? *Renew Sust Energy Rev* 62:134–163. <https://doi.org/10.1016/j.rser.2016.04.016>

- Rosillo-Calle F, Woods J (2012) The biomass assessment handbook: bioenergy for a sustainable environment. Earth Scan
- Shafiee S, Topal E (2009) When will fossil fuel reserves be diminished? *Energy Policy* 37 (1):181–189. <https://doi.org/10.1016/j.enpol.2008.08.016>
- Tiwari GN, Mishra RK (2011) Advanced renewable energy sources. RSC
- Toka A, Iakovou E, Vlachos D, Tsolakis N, Grigoriadou A-L (2014) Managing the diffusion of biomass in the residential energy sector: an illustrative real-world case study. *Appl Energy* 129 (0):56–69. <https://doi.org/10.1016/j.apenergy.2014.04.078>
- Utama NA, Fathoni AM, Kristianto MA, McLellan BC (2014) The end of fossil fuel era: supply-demand measures through energy efficiency. *Procedia Environ Sci* 20(0):40–45. <https://doi.org/10.1016/j.proenv.2014.03.007>
- Vertes AA, Qureshi N, Blaschek HP, Yukawa H (2010) Biomass to biofuels. Wiley, U.S.
- Wan Omar WNN, Amin NAS (2011) Biodiesel production from waste cooking oil over alkaline modified zirconia catalyst. *Fuel Process Technol* 92(12):2397–2405. <https://doi.org/10.1016/j.fuproc.2011.08.009>
- Yan S, Lu H, Liang B (2007) Supported CaO catalysts used in the transesterification of rapeseed oil for the purpose of biodiesel production. *Energy Fuel* 22(1):646–651. <https://doi.org/10.1021/ef070105o>
- Yusuf NNAN, Kamarudin SK, Yaakub Z (2011) Overview on the current trends in biodiesel production. *Energy Convers Manag* 52(7):2741–2751. <https://doi.org/10.1016/j.enconman.2010.12.004>