ENVIRONMENT FRIENDLY RENEWABLE ENERGY FROM BITTER ALMOND OIL

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95/FBAS/MSES 04

A dissertation submitted in partial fulfillment of the requirements for the

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DEDICATION

I dedicate my work to my beloved Mother (late), my Father, Brother, Sisters and especially my Husband Fiaz ur Rehman who encouraged and supported me during my entire study.

DECLARATION

I Zainab Tariq) (95-FBAS/MSES/F09), student of MS in Environmental Science session 2009-11, hereby declare that the matter printed in the dissertation titled“ Environment Friendly Renewable Energy from Bitter Almond Oil” is my own work, except where otherwise acknowledged and that dissertation is my own composition. No part of the dissertation has been previously presented for any other degree.

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FORWARDING SHEET

The thesis entitled **Environment Friendly Renewable Energy from Bitter Almond Oil"** has been completed by **Zainab Tariq (95-FBAS/MSES/F09)** in partial fulfillment of MS in Environmental Science has been completed under my guidance and supervision. I am satisfied with the quality of student's research work and allow her to submit this thesis, for further processes per IIU rules and regulations.

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ABSTRACT

The utilization of non-edible feedstock for biodiesel production attracts much attention owing to the issue with regards to avoiding a threat to food supplies. In this study, the optimization of biodiesel production parameters from bitter almond oil (*Prunusamygdalas* var. *amara)* in comparison with fresh vegetable Oil (FVO) and waste Vegetable Oil (WVO) was carried out. The free fatty acid value of Bitter Almond Oil (BAO) was found to be 0.8%, executing the one step alkaline transesterification method for converting Bitter Almond and vegetable oil fatty acids to their methyl esters possible. The optimum production parameters: catalyst amount, alcohol amount, temperature, agitation speed and reaction time were determined experimentally and found to be: 1.0 % by wt KOH catalyst amount and 0.9 wt% NaOH; 30ml,21ml and 16ml methanol amount according to 5:1,7:1 and 9:1 ratio respectively at 60°C-65°C reaction temperature, 300 rpm agitation rate and I hr reaction time. With these optimal conditions the conversion efficiency of BAO was 90%. The properties of the Bitter Almond biodiesel that was produced were observed to fall within the recommended international biodiesel standards. A review on GC analysis and FTIR results of this study shows that all its chemical and physical properties suits Bitter Almond non edible feedstock best to be utilized for biodiesel production.However, Bitter Almond feedstock is required to be cultivated abundantly on vast waste agricultural lands which are quite available in Mediterranean areas of Pakistan for its commercial use as biodiesel.

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"He who does not thank to people is not thank to Allah"

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ZAINAB TARIQ

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ABBREVIATIONS

ASTM	The American Society for Testing and Materials
WCO	World Customs Organization
FAO	Food and Agriculture Organization
UNEP	United Nations Environment Programme
HHVs	Higher Heating Values
MJ/kg	Megajoules per kilogram
cSt	CentiStokes
FAME	Fatty Acid Methyl Ester
GC-MS	Gas Chromatography & Mass Spectrometry
FT-IR	Fourier Transfer Infrared Spectroscopy
Tce/a	Total Energy Consumption Per Acre
MT	Metric ton
MMT	Millions of Metric Ton
AEDB	Alternate Energy Development Board
TCF	Trillion Cubic Feet
BOPD	Barrels of Oil per Day
MMFCD	One Million Cubic Feet Per Day

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I. INTRODUCTION

Energy resources are the most fundamental requirement for human existence. However, due to burgeoning population, industrialization, demand of fossil fuels, change in human life style, and economics of fossil fuel production require diversification of energy dependence. Industrialization although coupled with widespread use of fossil fuels in both industrialized and newly developing economies, has not only provided jobs to the population but has also generated an enormous amount of waste and emissions to the human environment. This phenomenon has resulted in highest consumption of fossil fuel so reducing the available reserve depletion but environmental degradation, as a consequence too. The highly industrialized countries, i.e., United States, Japan, China, and India are consuming a vast amount of fossil fuel resource with United States being the leader in consumption. However; renewable alternatives are also being explored in these economies.

Industrialization in Pakistan and with highest population growth, energy crisis has also become imminent. Although, Pakistan consumes more than 0.35 million barrels oil per day, it is ranked as 38th in the world oil consumption (Dawn, 2008). Due to highest bill to import oil from external source, it is important to develop renewable energy sources through agriculture biomass, sunlight and wind. In addition, the limitation of available sources for petroleum exploration is a strong motivation to focus on renewable energy. Furthermore, in order to explore fossil fuel reserves, use of coal and its gasification, or nuclear option are entangled with global political repercussions. In addition, environmental problems, i.e., degradation of air quality due to emissions caused by their use, draws attention to renewable fuel sources as an environment friendly alternative resource (World Energy Survey, 2004)

Pakistan with highest population growth but with enormous plant biomass requires exploring cheap energy production. Plant Biomass for biofuel has become an answer addressed by a growing number of researchers in both developed and developing countries due to its low production cost and with similar quality as crude oil. Production of energy from plant biomass has been proven cheap and is represented as Biofuels (Hisham, 2008).Biofuels derived in some way from plant biomass are considered as good renewable source to create alternative fuels. As compared to conventional fuels, biofuels are considered as an environment friendly fuel includes biodiesel, methanol, ethanol, etc. and are produced by using biomass, waste oil and vegetable oil, and other biomass sources (Demirbas, 2008). It is estimated that the use of biofuels in transportation industry is ~ 2% and this reached up to a production of 5 billion $ by year 2007. (Biofuels Facts, 2010).It is also estimated that it can meet 25% of world demand for transportation fuels by 2050 (Refaat, *et al.*, 2008)

Diesel fuels commonly called as *petro-diesel* play a vital role in industry, transportation and in energy generation. However its demand, cost and environmental impact has necessitated the exploration of biodiesel production from plant biomass. Bio-diesel has been produced from various sources and has been excavated for its fuel properties in its pure (100%) form and has also been blended with petro-diesel. Bio-diesel is denoted as diesel from biological source and is made up of alkyl esters of fatty acids attached to glycerol and also known as Fatty acid methyl esters (FAME) (Michael, *et al.*, 2005). The American Society for Testing and Materials (ASTM) defines "biodiesel fuel as mono alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat". Biodiesel is less toxic, biodegradable and has the lowest emission, if compared with petro-diesel. On the other hand, as compared to other alternate fuels, i.e., Liquefied Petroleum Gas (LPG) and hydrogen, have with less efficiency of engine and are not easily available everywhere. Due to global price increase in petroleum and its availability for growing industry, the government and private sector is taking interest in reducing dependency on petroleum and exploring the possibilities to convert low cost agricultural feed stock, wasted crops, oil-producing seed and waste edible oil to a more useful byproduct through trans-esterification with different catalysts (Ayhan, 2002). Biodiesel production depends upon the cost of raw material, i.e., supply of vegetable oil or other plant sources containing oil. However Biodiesel production cost by using pure vegetable oil and its availability is a question mark because of food supply issues in the world (Demirbas and Lin, 2009; Connemann, 1998). Strategies for cheaper biomass or crops from non-edible source are being explored in advance countries. Non-edible oil crops mostly, grow on wastelands and do not need intensive care as well as tolerated to drought and dry conditions (Leung, 2010). Therefore, the current trend all over the world is to encourage the propagation of such crops that could produce high amount of non-edible oil which could be used for the production of biodiesel. Non edible plants like *Jatropha*, have been under constant investigation for their potential biodiesel production. However, such plants are exotic to Pakistan and could result in disturbance of biodiversity.

Bitter Almond Plant *(Prunusamygdalus)* is a wild almond variety mounting in Balochistan and some parts of KPK. It is non-edible and can be a significant source for biodiesel production as an alternative to conventional fuel energy resources. It contains amygdaline and other chemicals, i.e., benzaldehyde and hydrocyanic acid produced through glucose-enzyme reaction and turn it into bitter product which is non-edible. Furthermore, due to its cyanide content, the human ingestion of more than 7.5 ml of bitter almond oil can be lethal (Gordon, 2011).Due to such reasons, its edible use and the cosmetic industry in the United States is banned, thus making it more suitable to be used for renewable fuel production which can be grown on dry waste lands.

The Almond Tree (*Prunusamygdalus*) with family Rosaceaeis a native to the Mediterranean climate region to Middle Asia (Pakistan Eastward to Syria and Turkey). Pakistan is one of the major almond-producing countries. Global Production of almond has increased 45% to a total yield of 1,837,566 MT or 4 billion lbs. in the last decade. (FAO, 2002). Its yield averages about 930 lbs. /acre, but can reach upto 3500-4500 lbs. /acre in some countries. Pakistan amongst top ten almond producers contribute with an average yield about 30,900 ton per anum over 7,500 hectares in Northern areas and requires least maintenance cost other than crops cultivated commercially (Livestrong, 2009)*.

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*Livestrong achieves. (2008) "Bitter Almond Oil and its Essentials". http://www.livestrong.com/article/260879-nutritional-value-of-raw-almonds

However wild or bitter almond (*Prunusamygdalus* var. amara) are the one which due to a genetic mutation in almonds produces bitter content, hence making it inedible due to the presence of toxic poisonous material. It has been reported that the seed of bitter almond tree produces~ 50 % bitter almond oil (BAO) with a pungent taste (Dorado, 2008). This BAO pressed from almond tree fruit could be a useful feedstock for biodiesel production since the crop is under-utilized and commonly produced on wastelands in wild.

Significance of study

A significant amount of work has been carried out to explore renewable energy by using non-edible crops containing oil. Biodiesel production is becoming a popular alternative to run diesel based vehicles in today's higher energy cost economy in both developed and under developed countries. However in Pakistan, where the economy is based on imported petroleum oil, there a need to explore alternate energy resources. BAO use for biodiesel production could become an additional innovative and logical step to promote a new renewable plant biomass source for fuel energy and progressive step towardssustainable environment. The process of biodiesel production requires the reaction of oil in presence of alcohol and catalyst. Biodiesel performance has been evaluated in diesel engine with promising results. Therefore the use of such non edible plants and its conversion to useful energy source could reduce the dependency of Pakistan on conventional fuels. It would be a clean biodegradable fuelresourcehat wouldcause less environment degradation when compared with conventional fuels. By commercialization of this possible fuel resource by establishment of trans-esterification plants for non-edible biomass could reduce the dependence of Pakistan on petroleum import. Moreover, its production and use would mitigate the effects of waste generation and greenhouse gas emissions, as a whole. Furthermore, it will make best use of the waste lands for massive production of fuel crops and subsequently, will help to reduce air pollution along with the associated health risks to the public with very low maintenance cost. It will not only bring agricultural communities closer but will generate job opportunities with ecological and economic sustainability.

In the view of literature on biodiesel research although a lot of work has been done on plant based oil resource throughout the world but little work has carried out on nonedible oil usage as renewable energy resource. According to my knowledge no work has been done on Bitter Almond Oil for biodiesel production in Pakistan particularly in Indo Pak subcontinent generally. Pakistan being among top ten producers world wide could trigger use of wildly grown bitter almond seeds for biodiesel production in order to overcome environmental and health hazards in shortage of fossil fuel energy. In view of this, the proposed study was designed as the first step towards this technology. In order to optimize and characterize biodiesel production from bitter almond oil, the following objectives were set for the study.

Objectives

- ✓ To produce optimum yield of biodiesel from non-edible Bitter Almond Oil (BAO) and compare its production with fresh edible oil (SVO) and waste vegetable oil (WVO).
- ✓ To analyze the Bitter Almond Oil biodiesel for fuel properties in accordance with ASTM standards for its practical application.
- ✓ To study physico-chemical properties of Bitter Almond Oil biodiesel and to compare them with other oil sources.

Justification of study

Pakistan is energy deficient and its economy and growing population depends up on import of petroleum and furnace oil from external sources. On the other hand, Pakistan being an agricultural economy produces a variety of non-edible plant biomass. This research was aimed to convert this biomass and waste oil into a useful commodity. It was an effort to develop a process at pilot-scale conversion of non-edible oil into biodiesel from BAO and study the feasibility for a large-scale cooperative facility to reduce fuel energy crisis in Pakistan. The other uses of bio-diesel were also kept in mind that include, the use of biodiesel in domestic or commercial generators, domestic use in stoves, and to overcome consumer problem on availability of an alternate fuel. Furthermore, pilot plants based on current procedure could be installed with a medium size or larger facility to produce biodiesel near the farms could be designed with an automated systems for maximize production efforts and to utilize raw biomass. In addition, other by-products during biodiesel production, i.e., glycerin and soaps, could be utilized for new market. By introduction of such products in industry or markets could make the production of biodiesel more affordable.

II. REVIEW OF LITERATURE

2.1 Historical background:

Biofuel production is in debate for a good period of time in the Western World especially due to dependence on Gulf Oil reserves. Furthermore, industrialization and excessive use of fossil fuel has segregated the civil society, general public, industrialists and policy-makers due to environmentalist movement on fight against climate change.

Biodiesel is produced by trans-esterification process carried out on vegetable oil, waste oils and other oil-producing biomass (Zhang, *et al*., 2009). The history of trans-esterification process for triglycerides can be traced back as early as 1853. However, diesel engine invented by a famous German, Rudolph Diesel (1893) started to run vehicles on peanut or vegetable oil till the alternative petroleum diesel was produced, that took over biodiesel due to low price, diesel availability and government subsidies. However, vegetable oil was in use as alternate oil till 1940's.The fuel shortage in 1970's Oil Crisis revived the interest of the Industrialized developed world for the alternatives. For this purpose, Scientists deliberated a conference in 1982 on the use of vegetable oils as fuels (ASAE, 1982) and discussed its different aspects related to cost of biofuel production, feedstock, oil-producing seed, extraction of oil, purification, effects on diesel engine, and fuel specification were discussed. But later on political-economy and industrial-government relationship dominated the decisions and resulted in limited work for Biodiesel industry (McDonnell, 1998).

However recently, due to fast rate of environmental degradation concerns global summits have deliberated on controlling of climate change and subsequently, this debate has re-incarnated the development of safe alternate fuels like biodiesel. In taking lead, European Union (EU) enacted certain subsides to Industrialist, i.e., 90% tax reduction to the biofuel producers, and users in Industry. Although vegetable oils has been used as potential candidate, but their high viscosities, low volatilities and other physical and chemical properties related to engine have been studied and rectified (Goering, *et al.*, 1982) but still cost of biodiesel production is still under research.

2.2 Biodiesel: A Renewable Resource

Biodiesel (BF-100) is also referred to as free fatty acid methyl esters (FAME), produced by trans-esterification of vegetable or plant oils. It can be used as a pure biodiesel (BF100) in diesel engine with slight modification or can be mixed with petro-diesel with different percentages. Its physico chemical characteristics are similar to petro-diesel and have less exhaust emissions. Its fuel properties as well as its environment-friendly nature are due to its easy bio-degradability, less toxicity and non-carcinogenicity (Martini &Shell, 1998). Therefore, Biodiesel has more environmental benefits due to its renewable substrate, i.e., fatty oils derived from rapeseed, soybean, palm, sunflower, coconut, linseed and other oil bearing seeds (Ma, *et al.*, 1999; Ksorbitz, 1999). Apart from having comparable fuel properties with petro-diesel, biodiesel is proven as a cleaner fuel as it reduces the detrimental gas emissions (Leduc, *et al*., 2009). This serve as the most talked about advantage amongst civil society. In a study, comparing compression-ignition properties for diesel engines, these advantages have been proven (Dorado, 2004). In recent years the systematic efforts have been made to utilize vegetable oil from palm, rapeseed, soybean, peanut, and other oil-bearing seeds. Such beneficial properties and environmental advantages are due to the presence of biodegradable organic compounds made of simple chain compounds (short-chain Fatty Acids) attached to glycerol to form triglycerides in biodiesel. On the other hand, petro-diesel is a mixture of non-organic compounds with variable complex carbon chains and with slow biodegradability (Srivastava *et al*, 2008). However, oils extracted from such crops have short-chain fatty acids with variable degrees of saturation and presence of oxygen. Therefore it results in low heating value (~10% less than petro-diesel), higher viscosity, and low molecular mass and less complex chemical structure. Other physical properties, i.e., cetane number, cloud point and pour point are higher as compared to petro-diesel (Barnwal, *et al.*, 2005). Beside that the economic feasibility for input cost in biodiesel production is high as feedstock account for about 80-85% of the cost (Imahara, *et al.*, 2006).

Biodiesel is non-flammable when compared to petro diesel, has similar viscosity if properly optimized, and is non-explosive with higher flash point (423 K as compared to biodiesel with 337 K). Furthermore, It is free of sulfur and benzene, a proven carcinogenic and more importantly, it is derived from renewable recycled resources (Yamane, 2001). It has been found to contain less sulfur, higher cetane number with excellent lubricating properties. In addition it reduces wear and tear in fuel system that results in enhancing the life of the fuel injection system (Imahara, *et al*; 2006).

Apart from all negative characteristics, the emissions produced from biodiesel are much reduced and more research in finding better product is in progress to find better production (Peterson,et al., 1991). The relative emissions of biodiesel as compared to petro-diesel are depicted in Figure 2.1.

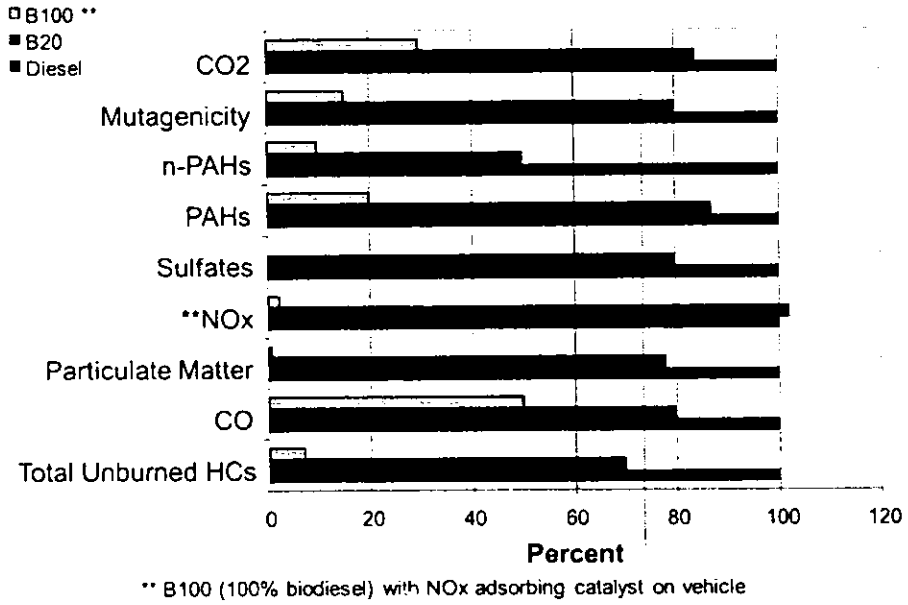

Figure 2.1 Relative emissions: Petro Diesel and Biodiesel

It has also been reported that pure biodiesel (BF100) with proper optimization produces less particulate matter (PM) with Carbon Monoxide (CO) emissions (<45%), Hydrocarbon (HC) emissions (<70%), however, an increase in NO_x emissions (> 10%) has been mentioned. It is due to relatively a high flash point (Anon, 2002).

2.3 Biodiesel Feasibility and Economic benefits:

Before discussing biodiesel feasibility, it is imperative to consider the burgeoning population in the South and the use of agriculture produce in biofuel production. One school of thought fears it as a threat to World food security especially in South, and a strategic challenge to the achievement of Millennium Development Goals to feed the malnourished population (UNEP, 2009). On the other hand, to meet the worldwide demand for energy, researchers need to sort out ways of increasing production from both current and new sources of energy. There are several aspects to take into account like cost, efficiency, feasibility and environmental effect according to a country's economy and environmental status.

Although biofuel production and its environmental and economic benefits have become an attractive paraphrase to civil society and policy makers, the cost of biofuel production depends on geography, area under cultivation, types of crops, feedstock availability, rainfall pattern, feasibility of crop and other factors. Amongst these, the cost of biodiesel, however, has remained the major obstacle in commercializing this notion when compared with petro-diesel price (Zhang, 2003). Not only the high cost of feedstock is a hurdle but its availability and conversion rate to biofuel is under intensive study. Trans-esterification process, its high-demanding major reactions parameters and quality control are few areas of concern (Hanna, 1999).

Although the global investment into biofuel production has crossed $5 billion mark worldwide, however, crop yield and availability of feedstock continuously, have phenomenally decreased due to climate change pattern, man-made disasters, natural catastrophes, etc. in the past decade has slowed down the progress in this area (UNEP, 2008). The most desirable but expensive feedstock for biodiesel production is seed-oil bearing crops with virgin oil available for mass production Moreover, economic benefits of biodiesel production could translate into generation of more rural-based jobs, fewer migrations to urban centers, and an increase in income generation for both producers and governments in taxes, and consequently results in lesser environmental degradation. However, an aligned agricultural policy to convert edible crops with subsidized cultivation of non-food crops will be required at governmental level though out the world without compromising the food supply to impoverished nations.

Furthermore, in future changes in the agricultural yields due to climatic conditions globally will define the degree to which edible crops to non-edible biomass can be supplied from existing cultivated land. In addition prices of agricultural commodity will be another determinant for future developments in this area (UNEP, 2008). As discussed previously, biodiesel production requires Oil tax exemption as practiced in European Union, which produces 89% of biodiesel worldwide. The largest consumer of petro-diesel, the United States of America, is behind Germany in terms of Biodiesel production and consumption, however, it would become the leading consumer by 2010(Ayhan, 2007).

2.4 Global Scenario:

Although biodiesel provides a ray of hope to overcome energy crisis globally, and in developing countries like Pakistan, there are various uncertainties attached due to population growth. European Union (EU) so far, has remained the largest market for consumption of biodiesel and has achieved reductions in emissions of carbon dioxide (CO_2) by 8%. Furthermore, EU has stipulated to convert transportation vehicle fuel to 10% by 2020. Similar changes are witnessed in United States of America and South

America.USA, Brazil, and the EU are the main biofuel producing countries. Ethanol from corn and sugar cane is widely produced in United States and Brazil, respectively. On the other side of Atlantic, EU has been converting rapeseed oil into biodiesel. Various countries have been consuming different feedstock to produce ethanol. Similar expansion in biofuel development and production has been witnessed in Asia, Africa and Oceania and South America (Figure 2.2).

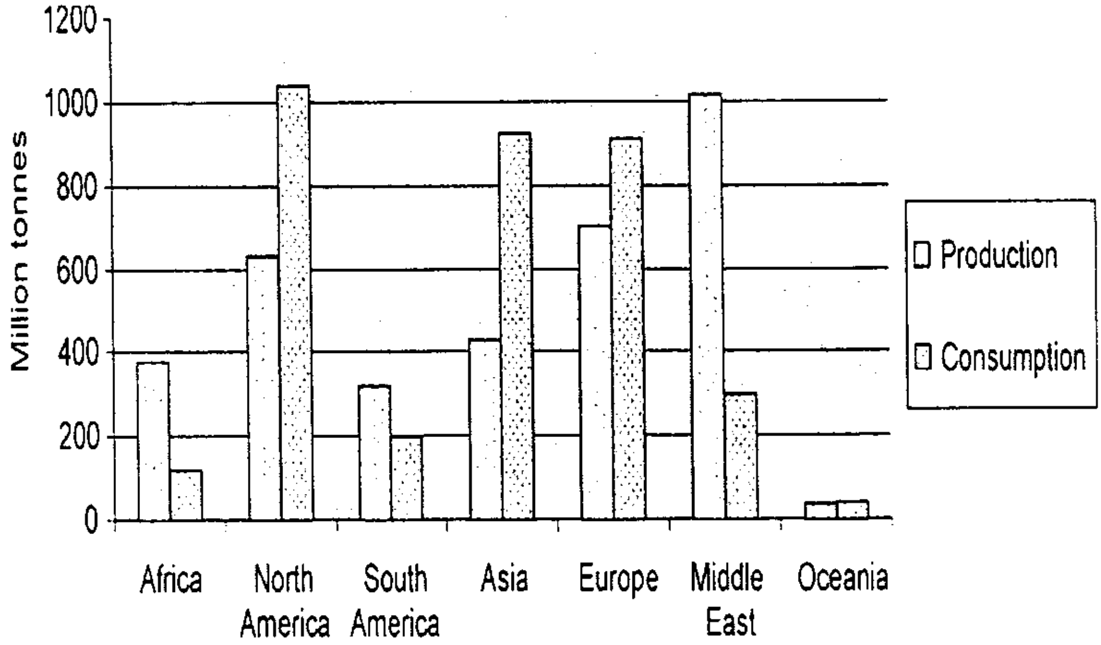

Figure 2.2 Oil production and consumption with regional distribution, 2002

However, South East Asian (SEA) region with highest population growth and largest chunk of existing population is still new to this concept of biofuel production. With rapid industrialization and energy demand, some SEA countries, i.e., Philippines, Malaysia and Singapore, are developing domestic markets for biofuels.

Power generation from hydel resource used to fulfill domestic requirements but more recently has dwindled down to < 30% due to silting of dams and reservoirs and also due to political incompetence in building new dams and industrialization. Therefore, oil yielding biomass from wasteland for biodiesel can be an imminent source for Pakistan as well. Small scale research for production and physico-chemical characterization is in progress in few educational and research institutes in Pakistan Ahmed, *et al.*,(2007)identified indigenous plant based biodiesel resources in Pakistan that includes castor, canola, mustard, peanut and soya bean oil, with the aim to develop cheaper and suitable raw materials and furthermore to conduct cost-benefit analysis (Wazir and Noshin, 2010).

2.5 Biodiesel and Economic Revolution:

UNEP, 2008 reports that global production of ethanol has tripled between year 2000 to 2007 (17 to 52 billion liters) whereas, production of biodiesel has increased eleven-fold (1 to 11 billion liters) with biofuels altogether contributing 1.8% of the global transport fuel. It is predicted that similar pattern will continue with an estimated increase above 5-6%,andincrease in use of biodiesel from 1% to 1.5% by year 2015 (UNEP, 2008).

Policy makers at global and local level consider biodiesel a way to reduce air pollution by controlling greenhouse gas emissions, and to significantly cut in oil imports. However, stimulating domestic agriculture for feedstock supply with food security for population require amendments in lifestyle. In addition, consumer education, reluctance of oil supply companies, unimaginable feedstock prices and lack of government initiatives with favorable tax benefits for biodiesel supply are hampering market growth. (Frost &Sullivan,2009)*. Adaptations of country's priorities with keeping in mind the economic benefits and ecological problems at both global and local level scan reduce emission of greenhouse gases, and biodiesel could become a cheaper fuel for public Transportation system. This way, the replacement of petro-diesel with biodiesel can effectively solve economic problems as well as energy deficiency in developing countries. EU has been promoting biodiesel and other alternative fuels in transport sector and has set to achieve increase in biodiesel use to 20% by 2020 (Lebrdevas and Vaicekauskas, 2006).

Similarly, the establishment of biodiesel market in the US is in its earlier stage and biodiesel is blended with petro-diesel to a 20% level or below. In terms of most common crops used for biodiesel production in US is soybean oil. On the other hand, rapeseed is in utilization and has expanded rapidly in Europe (Borgman and Deere, 2007).

2.6 Emissions from Biodiesel and Effects on Environment:

Temperature raise on the Earth's surface has been attributed to atmospheric carbon dioxide concentration due to continuous burning of fossil fuels, and in turn through emissions from industry, vehicles and natural phenomenon during the past couple of centuries (Federov, *et al.*, 2007). Different fossil fuels are made up of hydrocarbons in variable amounts and their

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*Frost and Sullivian, (2009) "The Attractiveness of Biodiesel amidst the Global Downturn". http://www.frost.com/prod/servlet/research continued use has changed the carbon balance in the environment. It is evident that an increase in CO_2concentration in atmosphere traps Ultra violet radiation resulting in extreme global temperatures, resulting greenhouse effect ultimately causing global warming (Crabbe, *et al.*, 2001). However, in recent times, depletion of fossil fuels and their limited availability in near future is the major driving force behind exploring alternate fuels to run an economy. Furthermore, due to environmental and atmospheric concerns, search for finding substitute fuels, that could be renewable, sustainable and environment-friendly, has become an imperative. Due to the absence of technology and continuous industrialization in developing countries, indigenous resources such as biomass for biofuel generation could be a solution. It includes production of ethanol, synthetic fuels, biodiesel and biogas. However, production of these fuels necessitates certain modifications in the product before their use (Barnwal and Sharma, 2004). It might include blending with petro-diesel for optimum results, or addition of certain chemicals and additives to increase fuel efficiency.

Biofuels are renewable energy resource due to their origin from biomass, a product of photosynthesis process. Different agricultural feed stocks are processed into biofuels or biodiesel, in particular, and bring both sustainable socio-economic development and environmental advantages. Their use reduces waste generation due to their degradability thus reducing the danger of soil fertility loss, and limited contamination of ground water resource. Furthermore, on vehicular engine level, it is suitable for catalytic converter, enhances engine life; 78% reduction in CO_2 than petro-diesel. More importantly, technology for establishment of biodiesel plant is easy to design, and is comparatively simpler than expensive petrochemical (Biofuel guide, 2008)*.

It has been evident that biodiesel could be blended with petrodiesel with various concentrationB10, B20, B50 (biodiesel 10%, 20%, 50%) without reducing its efficiency and could decrease emissions, as well. Hence, biodiesel use positively affects the atmosphere as a whole with enhancing the cycle of ozone formation. In addition, without compromising fuel and lubricating quality, biodiesel blended fuels reduces, sulfur (SO_x), Nitrogen (NO_x) and Volatile organic compounds (VOCs) and particulate matter, due in part by complete combustion (Holcapek, *et al.*, 2001). However, catalysts used in conversion or transesterification process and their deposition in the engine are of great concern. Biodiesel use can overcome sulfur emission as required by global environmental legislations. However, other poisonous byproducts such as lead has to be monitored that could be found due to contamination of biodiesel or FAME (Mittelbach and Tritthart, ,1988). Other poisonous substances of concern include, organo-metallic compounds, Silica, Manganese, Chromium, Ferrous, Nickel and others, that could be highly toxic even at low concentrations (Ferrari,2005)

2.7Limitation in Biodiesel Production& Use:

Apart from numerous advantages discussed in previous section regarding biodiesel production, few disadvantages that entail include: conversion of land from edible to non-edible crops; use of energy for producing high temperature during its manufacturing

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* Biofuel Guide, (2008) "Introduction to Ethanol and Biodiesel: A review. http://biofuelguide.net/category/bio-diesel/

process; its less suitability in low temperature environments; its impossible transportation through pipelines; a higher NO_x emissions; and corrosion of engines due to carbon deposition.

Furthermore, it is also evident that biodiesel attract more moisture than petro-diesel that could cause clogged engine in cold weather, and increases the risk of microbial growth in engine filters, as well. However, these disadvantages can be overcome by continuous research and modifications.

2.8 Raw Materials Used for Biodiesel:

Apart from raw material from meat tallow, or other animal sources, the most common crops used for biodiesel production include palm, rapeseed, soybean, canola, sunflower, coconut, wheat, barley, oat, rice, corn, groundnut, sorghum, sesame and poppy seed etc. along with other non-edible plants (Usta, 2005). However, due to the concern on compromise on food security issue globally, various other plants that have been under investigation for biodiesel production and are under intensive research are: marine microalgae, molds, Jatropha plant (*Jatrophacurcas*), Iroba (*Carapaguianensis*), Rubber plant (*Ficuselastica*), Hemp (*Cannabis sativa*), Tobacco and Fish oil (Pinto *et al.*, 2005).

In producing biodiesel, it is estimated that around 90% of the total cost is due partly for raw material (Connemann, 1998). Therefore, by growing non-edible crops from waste lands can solve this cost problem without any specific care (Leung, 2010). Few successful studies in India and Southeast Asia on biodiesel production from non-edible oils include; the use of Jatropha curcas oil (Patil and Yang,*et al;* 2009), Karanja seed oil (Meher, 2006; Karmee, 2005), Okra seed oil (Anwar, *et al;* 2010), Rubber (Ramad, *et al;* 2005 and Ikwuagwu 2010), Castor oil (Meneghetti, *et al;* 2006) and Mahua oil (Ghadge and Raheman, 2006).

Mustard plant has also been studied for its multiple advantages with high oil yield along with its cake containing effective biodegradable pesticide properties (Demirbas, 2008).

2.8.1 Lipids as Renewable fuel (Virgin and Non virgin Vegetable oil):

As discussed previously, the major resource for biodiesel production is vegetable oils due to their environmental benefits and availability. Its advantage lies in its renewability with its triglyceride content comparable to diesel fuel. It is estimated that global vegetable oil production has increased to more than 100 million tons with a matching a global consumption (Demirbas, 2005). Therefore, its diversion to the use of biodiesel production could jeopardize edible supply to growing population. Unless more land area is brought under oil-seed cultivation or its edible consumption is reduced, it would have negative impact. Other lipids that can be used to produce biodiesel are waste vegetable oil from restaurants and after domestic use, non-edible animal fats, non-edible plants *(jatrophacarcas),* castorseed and tallow (Demirbas, 2008). However, it all depends on the availability and indigenous production. In the United States, Soybean is the most-commonly used oil whereas Europe uses rapeseed oil for producing biodiesel. In Malaysia and Indonesia, coconut and palm oils are the major feedstock for its production (Sarin, *et al.*, 2007).

Waste vegetable oil (WVO) is gaining popularity among folks driving vehicles with modified diesel engine due to its low cost in biodiesel processing. However, WVO requires proper treatment through catalyst (Smith, 2010)*. Waste vegetable oil (WVO) is left over or waste oil from restaurants or other food processing industry involved in deep frying. It is typically collected free of charge in large drums by industry and transported to animal feed manufacturing, cosmetics industry, and other byproducts manufacturing (Whipnet Technologies, 2010). In order to convert WVO into biodiesel, the viscosity must be lowered by heat treatment; otherwise incomplete combustion and carbon deposition damage the engine. Furthermore, due to its viscosity and lower oxidative stability, more treatment is required as compared to fresh vegetable oil (Mittelbach and Tritthart, 1988).

With some alterations helped along with the use of additional ingredients, WVO is a cheap source to transform into biodiesel can be used as fuel with no problems. There are instances where WVO is used straight without any modification to it, however, run a vehicle on WVO only thing required is make a onetime modification to diesel engine to handle the properties of the WVO is required (Whipnet Technologies, 2010).

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* Smith, S.E. (2010) "Waste Vegetable Oil" The wise geek company and group traders http://www.wisegeek.com/what-is-wvo.htm

2.8.2 Algae: a renewable source for biodiesel:

Algae can grow in both saline and non-saline water in the presence of sunlight. It also contains fats or lipids along with CHO, Proteins and other micro and macro elements. Various algal varieties have been identified to contain ~ 40% of lipids contents (Becker, 1994). Therefore, it is under intensive investigation for biodiesel yield, as well. It is estimated that algae can yield 200 times more biomass than plant oils produced per acre Microalgae, being the fastest growing photosynthesizing organisms yield 46 tons of oil/hectare (Sheehan *et al.,* 1998). Recently, biodiesel production industry has started to undertake research in its economic feasibility.

2.9 Phyto-chemistry of Plant By-Products

Oil, lipids and fats inter-changeably represent glycerides of fatty acids and are insoluble in water but soluble in organic solvents (Anosike, 1994). Oils are triglycerides with attachment of fatty acids on Carbon Chain, where one or more fatty acid attaches to glycerol backbone and is denoted by mono-glyceride, di-glyceride or tri-glyceride. Sometimes they are also classified based on their degree of unsaturation (presence of double bond between adjacent carbons) as mono-, or poly-unsaturated fats, i.e., Lauric, Stearic, Myristic, Palmitic, Oleic, Linolenic, Linoleic and Arachidonic acids (Borgstrom, 1968). Global supply of lipids or fats or oils comes from vegetable sources that contribute ~68%, of total supply. Whereas, contribution of animal fat is also significant with 28 %, in addition to marine fat contributing ~ 4 % (Fox and Cameron, 1984).

For biodiesel production, it is important to study the composition of raw oil for their glyceride contents as well as, the degree of unsaturation. Experimental studies on biodiesel recognize the component of oil seed or lipids before its utilization in biodiesel production (Braverman, 1963). Various chromatographic and spectroscopic techniques, i.e., HPLC, GC-MS, FT-IR and NMR are used to identify and determine such compositions.

2.10 Trends in Biodiesel Research

The trend of biodiesel production as an alternative to the non-renewable fossil fuel has recently gained worldwide attention. Although quite significant work has already been done in this regard in the developed and developing countries like India and Brazil but in Pakistan the technology is still at the tentative level. Patil and Deng (2009) carried out comparative analysis of non-vegetable oils (Jatropa and Pongamia) and edible oils (Corn and Canola) for optimization of biodiesel production process. They analyzed different oil and fuel properties and also studied process's optimization parameters in detail.). Zhou and Thomson (2009) addressed the current status of biofuel in Indonesia, Malaysia, Philippines, China and India. They have given strategies, targets and polices in this regard.

Saydut *et al.,* 2008 extracted oils by solvent extraction method from Sesame plant (*Sesamumindicum* L.) growing in Anatolia Turkey and found that the methyl esters when transesterified showed improved fuel properties to be used as viable alternative to the petro-diesel.

Li *et al.*, 2009 investigated that marginal land utilized has great prospects to provide bioenergy in China. They suggested that plant like Salix, Hippophae, Tamarix, Caragena and Prunus can be grown in abundance that could provide 100 million tce/a in 2020 and 200 million tce/a in 2050. In another study, H_2SO_4 has been used as a catalyst to transesterify free fatty acids in the presence of triglycerides (~11% FFA, ~89% TG) which can covert >90% of free fatty acids (Marchetti and Errazu, 2008).

Jatropha plant has been under intensive investigation in India, Pakistan and elsewhere. Both quantitative and qualitative evaluation of the *Jatrophacurcas* components and its by-products during biodiesel production were extensively studied (Sotolongolo, *et al.*, 2002). It was found to contain excellent physical & chemical properties for biodiesel production. Similar studies on non-edible crops of Jatropha, Putranjiva and Karanja in India were carried out and the results were comparable for fuel properties as previously reported.
Bitter almond oil (BAO) for its potential has not been studied previously. However in a rare study conducted in Iran reported the potential of BAO when trans-esterified in presence of KOH (Atapour & Kariminia 2010). It was reported BAO to contain high amount of unsaturated fatty acids (84.7 wt. %) with low acid value (0.24 mg KOH/g).

However, food provision remained a major concern in mal-nourished Africa, Southeast Asia and elsewhere. Ewing and Msangi (2009) studied the importance of biodiesel production on food security since edible crops cannot be utilized if not in sufficient quantity. The food prices are expected to rise if biomass of edible crops is utilized in biodiesel production. For that purpose, agriculture development and income generation should be developed through biofuel advancement, so that purchasing by people can be improved.

Ahmad, *et al.*, (2008) carried out transesterification of oils for production and physiochemical characterization from peanut oil biodiesel. In order to optimize base-catalyzed transesterification process by using Safflower oil, temperature, oil to methanol molar ratio, type and concentration of catalyst were identified as source of variation in biodiesel production. It was concluded that molar ratio of Oil to methanol and reaction temperature was the main factors that affected the biodiesel or FAME production (Rashid and Anwar, 2008).

2.11 Pakistan: A Resourceful Country

Pakistan has a Diesel Consumption of 10 MMT, Petrol Consumption of 1.65 MMT and Total Import Value of Oil is US$ 6.60 Billion (Table 2.1). This shows that Pakistan needs to increase energy security by producing more energy in-house. A possibility through the development of Alternate Energy Sources, i.e., biodiesel production, wind resource energy, etc. is important to be considered.

Pakistan, being an agricultural country, consists of almost every conceivable type of natural habitats and it has been reported that there is more than 6000 species of flowering plants in Pakistan in four phytogeographical regions: Irano-Turanian (46%) followed by Sino-Himalayan (10%), Saharo-Sindian (9.5%) and Indian (4.5%).

Table 2.1 Pakistan Energy Scenario: A fact sheet (2005-2006)

	Oil	Gas	LPG	Coal	Electricity
Production Capacity	65577BOPD	3836MMCFD	1495MTD	4.06MMT	19,439MW
Remaining Reserves	324.47MMB	32.54TCF	______	185BT	______
Refining Capacity	12.88 MMT	______	______	______	______
Import	14.6 MMT	______	24779 MT	1.54 MMT	______

Though the Saharo-Sindian region occupies by far, the biggest territory, in terms of area, the density of uniregional elements is lowest in this region. In Pakistan 70% species are uniregional and about 30% of the species are bi- and pluri-regional (Ali and Qaisar, 1986). Being a floral emporium of such biodiversity, the geography and quality of soil, that could particularly suitable for different kinds of oil yielding plants. There is a need to study the potential for its resources for biodiesel production.

Alternate Energy Development Board (AEDB) Government of Pakistan has been established and has conducted various feasibility studies on alternate energy sources for Pakistan. Recently, experimental gas station with blended petro-ethanol (E-10) has been established. Beside ethanol related fuel development, biodiesel production and its experimental use in model villages run on biodiesel-run generators is under study.

Pakistan, being 6th largest country in population, requires continuous supply of cheap energy for its industry, domestic, agriculture and commercial consumers. Due to dependence on fossil fuels and their sharp rise in prices, it is becoming a harsh reality in most evident load-shedding and power outages all over the country. Technologically advanced countries are exploring alternate renewable energy sources for this upcoming shortage and so is Pakistan. Pakistan initially has an identity of an agriculture-based economy, is now growing to become an industrialized country. Energy requirements to run industry are also increasing. However, energy generation dependent on fossil fuel is taking its toll due to burgeoning oil prices coupled with politicized issues of hydropower generation. Alternate energy in the form of biodiesel at rural as well as small farm level can address this issue. As discussed previously, one cannot rely on imports for edible oil for this purpose. Exploring exotic Jatropha plants can be cultivated in Pakistan especially in saline soil with less quantity of water and it can also withstand high temperature. It yields up to 2tons oil/hectare. But as it is exotic and can cause damage to local flora and fauna. Therefore, utilization of waste land or wild oil-seed crops have the potential. If in ideal condition Pakistan all uncultivated land is employed for biodiesel production, 56 million tons of biodiesel per year can be produced, a huge amount, while present need of diesel fuel is about 8.5 million tons (Ministry of Petroleum and Natural Resources, Government of Pakistan). At national level, production of major stake approaches from cottonseed subsidizing 75% of the native production. Canola rapeseed and mustard give 15%, while safflower, sunflower, corn & soybean contribute the remaining 10%. Government of Pakistan has established the Department of Pakistan Oilseed Development Board (MINFA) is precisely solemn to upsurge the production vegetable oil. The Pakistan State Oil (PSO) devises and has taken initiative for its research and developmental work regarding biodiesel production project to encounter government's target of blending 5% biodiesel with petro diesel by 2015 and 10% by 2025 (Khan, 2007).

Pakistan's necessity for energy resources is rising and being an agricultural country, Pakistan is blessed with vast land for the cultivation of energy crops. The only thing requisite is the awareness for its dire need and will to meet the targets. Hence biodiesel production project has a very booming prospect in Pakistan and is quite feasible in practice. Raw material for biodiesel production can be obtained indigenously & notably Government of Pakistan is quite thoughtful in generating biofuel energy resources. Pakistan being agriculture based economy; biodiesel production in the country will employ a lot of jobless people, empower the farmers &reinforce our agricultural sector.

According to AEDB, known oil yielding plants in Pakistan that are feasible for biodiesel production includes Sun flower (*Helianthusannus*), Line seed *(Linumsitatisimum),*Pongame tree (*Pongamiapinnata),* Castor beans *(Ricinuscommunis),* cotton seeds *(Gossypiumhirsutum),* Olive tree *(Oleaferruginea),* Hemp plant *(Cannabissativa*), Oat plant *(Avenasativa),* Carthamus*(Carthamusoxycantha),* Safflower *(Carthamustinctorius),* Soybean *(Glycinemax),* Sesame plant *(Sesamumindicum)* and Rape seeds *(Brassicarapa).*AEDB is encouraging the small farmers to grow the required crops for the vegetable oil to overcome electricity shortage for their village (Jafar, 2010).

However, in Pakistan also, growing foods versus fuel debate, non-edible biodiesel feedstock are growing in popularity (Pokoo-Aikins,*et al.*, 2009). The second generation of crops denotes nonfood crops or nonedible plants having certain bitter parts that are bitter or containing non-edible content (seed oil) likely, waste biomass (nutshells), wood, etc (Biofuels guide, 2008).

2.12 Bitter Almond: Biofuel Feedstock

*Prunusamygdalus (*Bitter Almond) fruit contains a glycosidic compound known as amygdalin, which is major factor contributing to the bitter nature of almonds making it non-edible. Other compound such as hydrogen cyanide, a content of Almond seeds makes it poisonous and fatal if intake exceeds 7.5ml. As a word of caution, bitter almonds do contain cyanogenic glycosides in their bark and leaves as well if these are consumed in large quantities, they can cause convulsions and death. Such almonds are avoided but often adulterated with sweet almond oil for use in medicines and cosmetics. The oil yield of BAO is variable in different varieties and has been reported in the range of 45-50 %(Dorado, 2008).

2.13 Biodiesel Production and Quality:

Large, branched triglycerides are transesterified to produce Biodiesel comprising of smaller and straight chain molecules of methyl esters, consuming an acid or alkali enzyme as catalyst. This includes three stepwise process reactions with midway development of di-glycerides & mono glycerides giving rise to three moles of methyl esters while one mole of glycerol from triglycerides. The biodiesel production processes for are well acknowledged. Among those known methods, three basic ways to biodiesel production from vegetable oils are: Direct acid catalyzed transesterification of the oil, base catalyzed transesterification of oil and conversion of the oil to its FFA'S and later to biodiesel (Marchetti,*et al*; 2007).

Base catalyzed reaction is the most commonly route to biodiesel production and is done for several reasons which include its high conversion rate (98%) with minimal side product reactions and reaction time, low temperature and pressure requirement and direct conversion to biodiesel with no transitional compounds and non-participation of any exotic materials. Base catalyzed biodiesel production, the chemical reaction depicted below.

$$\begin{array}{l} CH_2OCO-R'''' \\ CH_2OCO-R'' \\ CH_2OCO-R' \end{array} + 3ROH \xrightarrow{CATALYST} \begin{array}{l} CH_2OH\ \ R'''COOR \\ CH_2OH + R''COOR \\ CH_2OH\ \ R'COOR \end{array}$$

100 pounds 10 pounds 10 pounds 100 pounds

Oil Alcohal (3) Glycerin Biodiesel (3)

Alcohols including Amyl alcohol, Butanol, Methanol, Ethanol and Propanol are employed in the transesterification reaction. Frequently used alcohols are Methanol and Ethanol though Methanol has become the major ingredient due to its low cost, and advantages related to its physico chemical properties. Sodium and potassium hydroxide with alcohols can readily react with triglycerides hence dissolving alcohols easily. It has been reported that molar ratio of alcohol to triglycerides obligatory for transesterification process is 3:1. Usually in preparation, the ratio prerequisites to be greater to lead the equilibrium to forward direction giving a maximum ester yield (Marchetti,*et al*; 2007).

Atapour & Kariminia (2010) studied and experimented selecting different oil to methanol ratios ranging from 3:1 to 11:1 and its effect on production of biodiesel. The stoichiometric ratio of alcohol to triglycerides stands 3:1, as transesterification is not an equilibrium reactions in order to shift the equilibrium in benefit of alkyl ester generation usually an excess amount of alcohol is used. It was perceived that with growing the concentration of methanol to oil molar ratio from 3:1 to 7:1, the biodiesel yield & purity augmented from 74.6 to 92.7 & from 68.4 to 90.9, respectively while the product yield was greater than before from 91.8 to 97.2. Consequently, the outcome of methanol to oil ratio on the yield of biodiesel and its purity is more than its influence on the yield of product. María *et al;* 2008) analyzed biodiesel quality and tested according to the standard [UNE-EN 14214, 2003] used automotive fuels. Fatty acid methyl esters (FAME) for diesel engines and followed requirements and test methods. Particular critical parameters interrelated with composition of the methyl ester of each biodiesel take account of cetane number, iodine value, oxidation stability & cold filter plugging point in accordance with two more parameters including degree of saturated and unsaturated long chain factors.

To operate diesel fuels without any troublesome, it is important to ensure that biodiesel that has been produced completes its transesterification reaction with aspect of removal of glycerin, alcohol, catalyst and absence of FFA. All above entailed parameters are specified through ASTM standards D6751 and should meet the identified standard of pure biodiesel B100 to be used as pure fuel or blended with Mineral diesel/Petro diesel(Anonymous, 2007).ASTM biodiesel specifications must be adopted in order to ensure the standard of generated fuel acquired from a resource. These specifications are mentioned in chapter 3.
An essential aspect of biodiesel making is its commercial production or the design of equipment and construction of biodiesel production facilities to be employed. A simple

production flow chart along with a short explanation of the steps involved to acquaint the reader with the general production process (Figure 2.3).

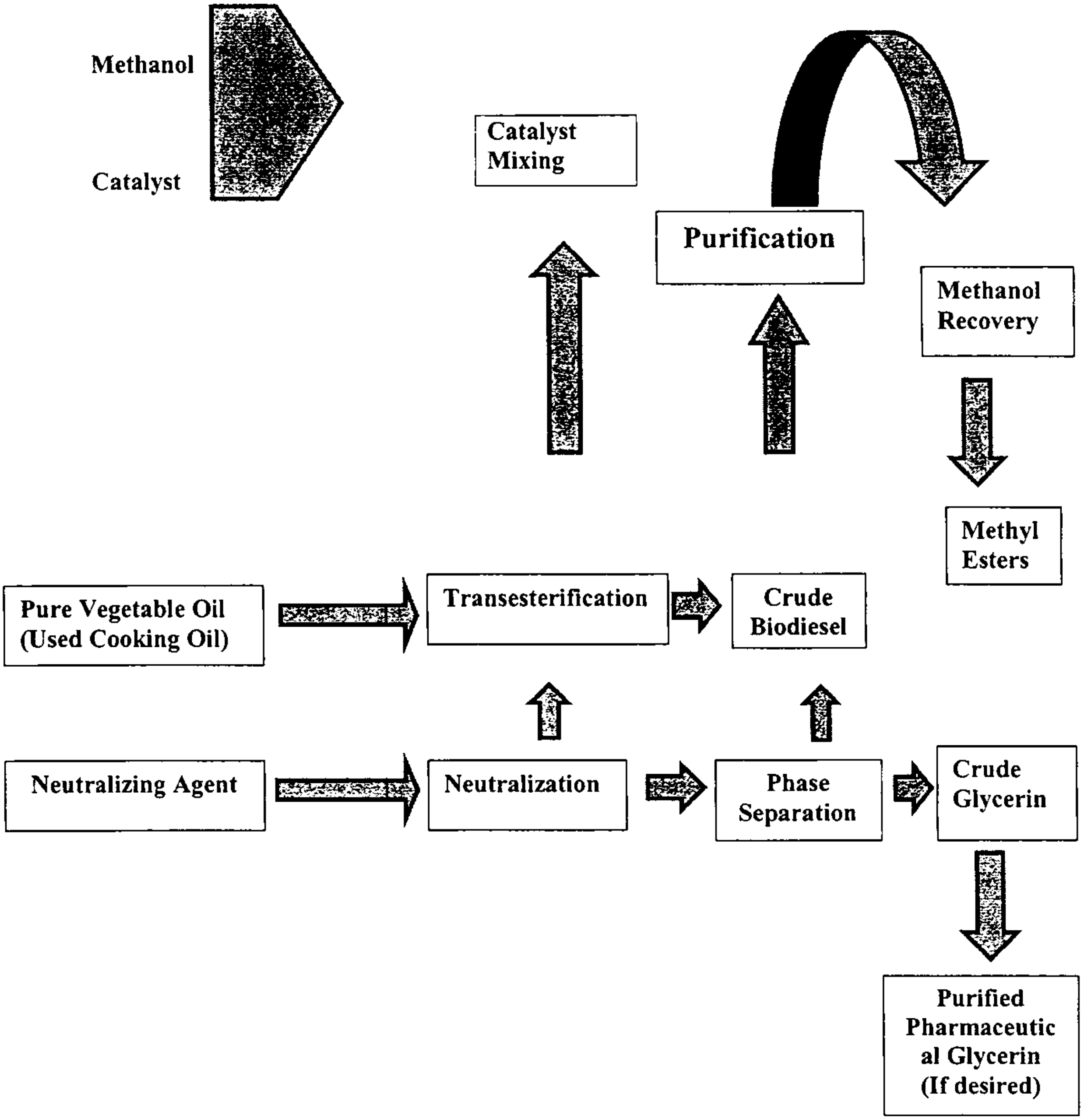


Figure 2.3 General Biodiesel Production Process

III. RESEARCH METHODOLOGY

The present research work was conducted during 2010-2011 in Biotech Laboratory, Department of Environmental Sciences, Faculty of Basic and Applied Sciences, International Islamic University Islamabad. The Research work was intended to fulfill the systematic work and Biodiesel production from plant biomass. Physico-chemical characterization and phytochemical analysis of Fresh vegetable oil FVO (unused), Waste Vegetable Oil WVO (used) cooking oil and oil from bitter almond seeds (pure plant biomass) with particular emphasis on *Prunusamygdalus* var. *amara* was executed in Biofuel Lab, Department of Plant Sciences, Quaid-i-Azam University, Islamabad, Department of Chemical and Material Engineering, National University of Sciences and Technology, Islamabad and Hydrocarbon Development Institute Program, Islamabad.

3.1. MATERIALS

3.1.1 Sample Collection:

Bitter oil from almonds was extracted from *Prunusamygdalus* var. *amara* of the Rosaceae family. It is a native to Mediterranean climatic region in Pakistan. It is mainly grown in Balochistan and NWFP because of its nurturing requirements that possibly meet in the particular environment. The Bitter Almond seeds bear an enzyme that contains amygdalin that decomposes into benzaldehyde, glucoside, and hydrocyanic acid (poison) making the seed non-edible (Dorado,2008). The normal yield of 40–45% through pressing practice can be obtained from shelled seeds of Bitter Almonds. It has a pungent blistering taste& is yellowish in color.

Newly cultivated crude bitter Almonds with nutshells were procured from shop of GanjKohati market of Peshawar. Although previously reported to produce 40-50% bitter almond oil (BAO), Five (5) kg of locally procured almond seeds yielded three liters (~ 60% by weight) of almond oil by using electric oil expeller (KEK P0015, 10127). Beside oil, two 2kg of oil cake was weighed and packed in plastic bags. For comparative studies, Straight Vegetable Oil (SVO) (unused cooking oil) was procured from local market. Same SVO was used for frying and as a result, Waste Vegetable Oil (WVO) (used cooking oil) was secured for comparative study against Bitter Almond Oil. Biodiesel yield from 3-sample types and their fuel properties were analyzed and compared.

3.1.2 CHEMICALS

Chemical used for Biodiesel production included Analytical grade Methanol (CH_3OH) (Merck Germany), Sodium Hydroxide ($NaOH$) (Merck Germany), Potassium Hydroxide (KOH) (Merck Germany), Acetic acid (CH_3COOH) Merck Germany, Isopropyl alcohol (CH_3-$CH(OH)$-CH_3), Phenolphthalein ($C_{20}H_{14}O_4$) Merck Germany, Anhydrous Sodium Sulphate (Na_2SO_4), Oxalic acid ($(COOH)2H_2O$) Merck Germany, and Distilled water.

3.1.3 INSTRUMENTS

3.1.3.1 Instrument used in Biodiesel production: Instruments used for Biodiesel production included electric oil expeller (KEK P0015, 10127), Hot plate (VWR, VELP

Scientifica), Magnetic stirrer (TEFLON), Titration apparatus, Electrical Balance (AND, GF-3000), Heat Oven (Merck Germany), and Micropipette (HUWAWEI, H 1000).

3.1.3.2 Instrument used in Phytochemical Analysis

Instruments used for Phytochemical Analysis included FT-IR (Fourier Transfer Infrared Spectroscopy), (Shimatzu, Japan), Electrical Balance (AND,GF-3000), Hot plate (VWR, VELP Scientifica).

3.2 METHODS

3.2.1 Procedure for Production of Biodiesel

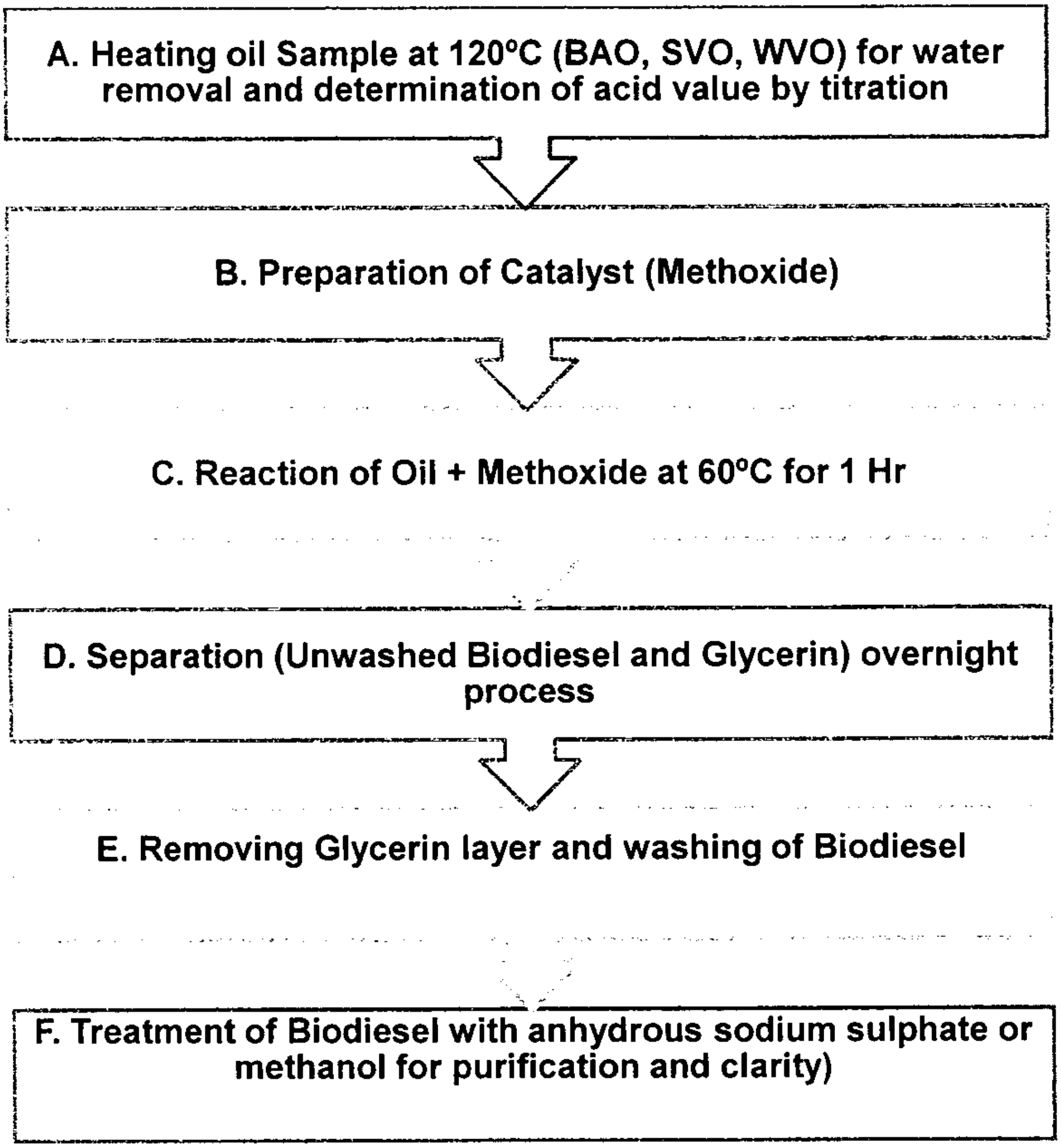
Three different (Oil to Methanol) molar ratios (5:1, 7:1 and 9:1) were optimized for biodiesel production with two catalyst, Sodium hydroxide (NaOH) and Potassium hydroxide (KOH) for comparative study. Every oil sample was first filtered to remove any suspended particles and debris by using Whatman no. 42 filter paper. Every filtered oil sample was heated on hot plate to evaporate any water contents and to turn oil sample less viscous. On the other hand, catalyst-methoxide (mix of catalyst and methanol) was prepared by taking 0.9g of NaOH and or 1g of KOH with Methanol conferring molar ratio of 5:1, 7:1 and 9:1 (measuring 30ml, 21ml and 16ml), respectively by using hotplate with magnetic stirrer. Before every treatment, the temperature of oil was brought to 60°C before methoxide was added to the oil. The reaction was carried out on hotplate with magnetic stirrer (300rpm) at 60°C for 1 hour. Transesterification process (Eq.1) was observed that began within first five minutes of mixing and resulted in layer formation with visible color change. Physical changes were observed throughout the reaction time.

$$\begin{array}{l} CH_2OO-R1 \\ CHOO-R2 \\ CH_2OO-R3 \end{array} + 3CH_3OH \xrightarrow{CATALYST} 3CH_3OOR_X + \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array}$$

Triglyceride ***3 Methanols*** ***Biodiesel*** ***Glycerin***

where, R1; R2, and R3represents fatty acid alkyl groups and oil source.

The Flow diagram figure 3.1 depicts complete biodiesel while the experimental protocols for all Oil samples along with methoxide are displayed in Table 3.1 – 3.2.



A. Heating oil Sample at 120°C (BAO, SVO, WVO) for water removal and determination of acid value by titration

B. Preparation of Catalyst (Methoxide)

C. Reaction of Oil + Methoxide at 60°C for 1 Hr

D. Separation (Unwashed Biodiesel and Glycerin) overnight process

E. Removing Glycerin layer and washing of Biodiesel

F. Treatment of Biodiesel with anhydrous sodium sulphate or methanol for purification and clarity)

Figure 3.1Protocol for Biodiesel Production

3.2.2Synthesis of Biodiesel

- The filtration was carried out by Whatman filter paper No. 42. Filtration depends on oil quality (thickness). After filtration the solid particle and impurities were removed from the crude oil.
- The oil was placed on hot plate and heated up to 120°C. As by raising of heat the water separated from oil and fall into the bottom, maintain the temperature of oil until no steam raised.

- Preparation of catalyst involves mixing of the required amount of Sodium hydroxide (NaOH) and Potassium hydroxide (KOH) with Methanol (CH_3OH) in a closed flask. It was placed on hot plate with magnetic stirrer and was done at room temperature at 300rmp. .

- Oil was kept in air tight vessel and placed on hot plate, and was heated to reach at 60°C. The prepared catalyst-Methoxide mixture was added to oil maintaining its temperature at 60°C. The reaction time for the mixture of Methoxide & Oil sample was allowed for 60 minutes at 300 rpm. Samples of BAO, SVO and WVO with 5:1,7:1 and 9:1 ratio were repeated at same temperature and time.

- Solution was settled for overnight and allowed to cool at room temperature away from direct light. Two products in the form of layers were observed. The upper clear transparent part was identified as raw Biodiesel (fatty acid methyl ester or

FAME) and a denser layer of a gelatinous mass, identified as glycerin, congealed at the bottom.

- Separatory funnel was used to assay the products. However, separation of biodiesel was also done by using pipette with pumping apparatus and more precisely by micropipette. The transparent biodiesel was drowned to a separate vessel. Glycerin was heated again, labeled, weighed and transferred to another separate vessel.
- Biodiesel was washed in a container with a valve of 10 inches from bottom. The container was filled half by warm water and rest to last valve by biodiesel then placed overnight for settling. The water and biodiesel were separated in few seconds. In first washing the residual dissolved in water which showed a milky color. The washing was repeated three times and weight of Biodiesel was recorded and has been reported in results.

- After washing of biodiesel access amount of residual water and Methanol were present. The residual water was eliminated by treatment with anhydrous Sodium Sulphate (Na_2SO_4), followed by filtration.

In next step the biodiesel sample was subjected to distillation at $60^\circ C$ with rotary evaporator under a moderate vacuum to recover the excess amount of methanol (Ahmed *et al.*, 2009). Conversion of Fatty acid methyl ester (Biodiesel) from triglyceride (Oil) was determined by the following formula:

$$Yield\ of\ Methyl\ Ester = \frac{Methyl\ Ester\ Produced\ (gms)}{Oil\ taken\ for\ reaction\ (gms)} \times 100$$

Table 3.1 Experimental protocol for Synthesis of Biodiesel from FVO, WVO and BAO with NaOH

Samples	Oil (ml)	MeOH (ml)	Catalyst (NaOH) grams/ml	Molar Ratio	Reaction Temperature
FVO_A	150	30	0.9	5:1	60-65°C
FVO_B	150	21	0.9	7:1	60-65°C
FVO_C	150	16	0.9	9:1	60-65°C
WVO_A	150	30	0.9	5:1	60-65°C
WVO_B	150	21	0.9	7:1	60-65°C
WVO_C	150	16	0.9	9:1	60-65°C
BAO_A	150	30	0.9	5:1	60-65°C
BAO_B	150	21	0.9	7:1	60-65°C
BAO_C	150	16	0.9	9:1	60-65°C

Table 3.2 Experimental protocol for Synthesis of Biodiesel from FVO, WVO and BAO with KOH

Samples	Oil (ml)	MeOH (ml)	Catalyst(KOH) grams/ml	Molar Ratio	Reaction Temperature
FVO_A	150	30	1	5:1	60-65°C
FVO_B	150	21	1	7:1	60-65°C
FVO_C	150	16	1	9:1	60-65°C
WVO_A	150	30	1	5:1	60-65°C
WVO_B	150	21	1	7:1	60-65°C
WVO_C	150	16	1	9:1	60-65°C
BAO_A	150	30	1	5:1	60-65°C
BAO_B	150	21	1	7:1	60-65°C
BAO_C	150	16	1	9:1	60-65°C

3.3 Determination of Free Fatty acid (FFAs) by Aqueous Acid-base Titration

The Free fatty acid number of oil was determined by aqueous acid base titration (komers *et al.*, 1997). Two type of titration were performed, blank titration and sample titration. In

Blank Titration only Isopropyl alcohol and phenolphthalein indicator were taken in flask and added sodium hydroxide and potassium hydroxide for the detection of free fatty acid of oil from burette to flask on oxalic acid, color was changed, indicating the end point. In Sample Titration Isopropyl alcohol, sample of oil and phenolphthalein as indicator were taken in flask, added sodium hydroxide and potassium hydroxide from burette, color was changed, indicating the end point. The free fatty acid number of oil was determined by the following formula

Free Fatty Acid Number = $(A-B)\ C / V$

Where: A = Volume of *Potassium hydroxide* used for Sample (mL)

B = Volume of *Potassium hydroxide* used for Blank (mL)

C = *Concentration* of Potassium hydroxide (g/L)

V = Volume of Sample

3.4 Determination of Acid Number by Aqueous Acid Base Titration

Aqueous acid base titration methodology was used for the determination of Acid number of biodiesel, similar to that used for the detection of Free Fatty acid number in oil. Both Blank and Sample titration were for the catalysts.

The acid number of Biodiesel was determined by the following formula

Acid Number = $(A-B)\ C/V$

A = Volume of Potassium hydroxide used for Sample titration (mL)

B = Volume of Potassium hydroxide used for Blank titration (mL)

C = Concentration of Potassium hydroxide (g/L)

V = Volume of Sample

3.5 Determination of Fuel Properties

Fuel properties of biodiesel obtained from different molar ratios of different oil samples were tested for Flash point (°C) by ASTM (American Standard for Material and Testing) D-93, Cloud point (°C) by ASTM D-2500, Pour point (°C) by ASTM D-97, Kinematic viscosity @ 40 °C by ASTM D-445, Density @ 15°C kg/h by ASTM D-1298, Acid no: mg KOH/gm by ASTM D-974, Color comparison, Iodine value, Sulfur content (%) wt by ASTM D-4294 and specific gravity respectively. Table 3.3 shows the specification for ASTM D6751-07a of Almond Oil.

Table 3.3 Properties of Almond Oil with specification for ASTM D6751

Fuel properties	**ASTM Method**	**Limits**	**Units**	**ALM OIL**
Kinematic Viscosity @40 °C	D-445	1.9 to 6	mm^2/sec	34.01
Density @ 15 °C Kg/L	D-1298	0.8343	g/cm^3	0.911
Specific gravity	--	0.851	-	0.887
Total Acid Number mg KOH/gm	D-974	0.50 max	mg KOH/gm	0.24
Color	Visual	--	-	Light golden
Iodine Value	--	--	$mg/I_2/g$	81.62

This table shows Bitter almond Oil properties in accordance with fuel properties according to ASTM D6751 standard. All the properties are within the range for specification with fuel properties that is Density@ 15°C Kg/L according to D-1298 is $0.911g/cm^3$, specific gravity (0.887) within the limit(0.851), total acid number mg KOH/gm (0.24) according to

D-974 except Kinematic Viscosity @40 ^{0}C being 34.01mm^2 /sec higher than the limit 1.9 to 6 max according to D-445 ASTM standard. Iodine value for BAO is also high being 81.62mg/I^2/g which proves its biodegradable nature and lesser shelf life.

3.6 GC and FTIR analysis:

Different analytical methods were investigated for fuel quality assessment and monitoring of biodiesel. These methods include FT-IR spectra interpretation (Figure 3.2) and a review on GC-MS analysis which were used for the verification of prescribed biodiesel standard. FTIR spectroscopy is an analytical tool in the quality control of edible and non-edible oils. This analysis was carried out at NUST University, Department of Material and Chemical Engineering, Islamabad. FTIR spectroscopy was used to monitor the products of transesterification of oil samples FVO, WVO and BAO in methanol to FAME or biodiesel. FTIR spectroscopy uses absorption bands within an IR range typically due to presence of functional groups e.g. –OH,C=O,N-H,CH_3 (Marc,2004) . On the other hand, GC analysis owns a technique in which nonvolatile fatty acids are altered chemically to the conforming volatile Fatty Acid methyl esters FAME. GC-MS is used usually for fat analysis. Gas chromatography spectrometry subsequently analyzes the volatile mixture (Greenlief, 2004).

For FTIR analysis standard sample of polystyrene is used in order to ensure that instrument is calibrated and working well. Then following the methodology a background of spectra for initial reading is assessed and then procedure for liquid samples like biodiesel samples a standard of NaCl pellet. for a drop of liquid sample is inserted between two pellets which is scanned for absorption bands in mid IR range of 4000 cm-1 to 450 cm-1. The former background spectra are then subtracted from the sample spectra. Instrument used for analysis was Perkin Elmer model spectrum 100 (Figure 3.2).

Most important thing is the correct interpretation of spectra showing different peaks in analysis within IR range using reference of Infrared Absorption Frequencies that would be used as a resource material to the spectrum observed (Appendix 4).

The quantity of FAME and its composition in biodiesel was evaluated and analyzed according to UNE-EN 14103 biodiesel test method, by means of a HP 6890 series model2 gas chromatograph with a FID.

Atapoura*et al*; 2010 studied the fatty acid analysis of Iranian BAO by GC-MS which showed that the contribution of unsaturated fatty acids in the bitter almond oil was containing Linolenic Acid, Linoleic Acid & Oleic Acid. Total fatty acids composed of saturated fatty acids entailing mainly stearic & Palmitic acid. The other components of in small amounts of the fatty acid composition were not determined. Greater unsaturated fatty acids content could cause a reduced cetane number& cloud point, while stability of the biodiesel generated is also affected.

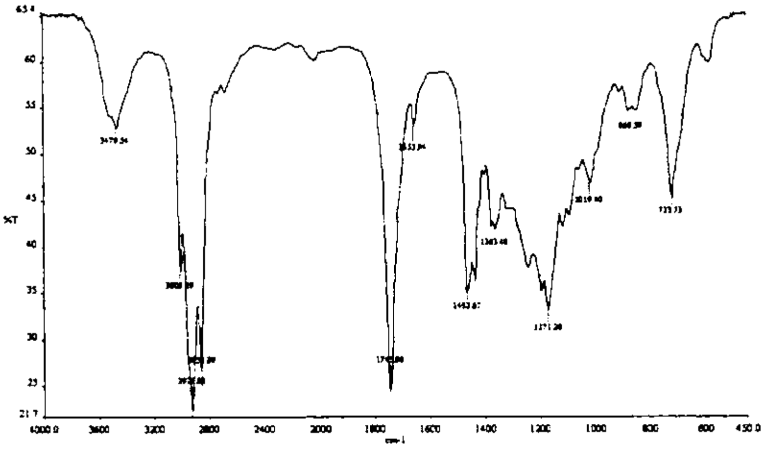


Figure 3.2 FTIR Spectra of Biodiesel from Bitter Almond Oil (BAO)

IV. RESULTS AND DISCUSSION

In order to characterize and optimize the biodiesel production from Bitter almond oil (BAO), the raw bitter almond (*Prunusamygdalus* var. *amara)* was dehulled and subject to extraction. Quantification of BAO was conducted and the raw oil was converted to biodiesel at the Department of Biotechnology, IIUI. Physico-chemical characterization and phytochemical analysis were compared with Fresh vegetable oil FVO (unused), and Waste Vegetable Oil WVO (used cooking oil). The FTIR of all samples were executed at the Department of Chemical and Material Engineering, NUST (National University of Sciences and Technology), Islamabad and HDIP (Hydrocarbon Development Institute Pakistan) respectively.

Biodiesel characterization is based upon various parameters, i.e., transesterification of samples with two catalysts with different concentrations, free fatty acid determination, acid number determination, and conversion rate of oil to biodiesel with various Oil to MeOH molar ratio, fuel properties and physico-chemical analysis & comparison with (American Standard Testing Material)ASTM standard, have been discussed in the following pages. Furthermore, biodiesel characterization by using FT-IR spectroscopy was also carried out. The details of results are systematically described in the following sections:

4.1 Effect of Methoxide optimization on Biodiesel Production

Transesterification or alcoholysisis the chemical process used for the making of Biodiesel or FAME from crude vegetable oil. Ethanol, Propanol, Methanol, Butanol and Amyl alcohol are most commonly used alcohols for transesterification process. For this study, the transesterification of oil samples was carried out in presence of methanol with Oil: MeOH ratio of 5:1, 7:1 and 9:1. MeOH was used to dissolve catalyst. i.e. NaOH and KOH crystals that formed a powerful methoxide solution. Previously, methanol has been reported often because of its low cost, its physical and chemical advantages, its capability to react with triglycerides (TG) rapidly and its dissolving property of alkaline catalyst (Ma and Hanna, 1999). The stoichiometric ratio for transesterification entails three moles of MeOH and one mole of triglyceride to produce three moles of fatty acid alkyl esters and one mole of glycerol (Meher,*et al.*, 2006).

Methanol to oil molar ratio is one of the most significant factor affecting the transesterification reaction (Banerjee and Chakra borty, 2009; Rashid and Anwar, 2008). Higher molar ratio results in a better ester conversion in a shorter time (Feuge and Grose, 1949). The effect of this parameter on the biodiesel yield and it's by- product yield is shown in Table 4.1& 4.2.

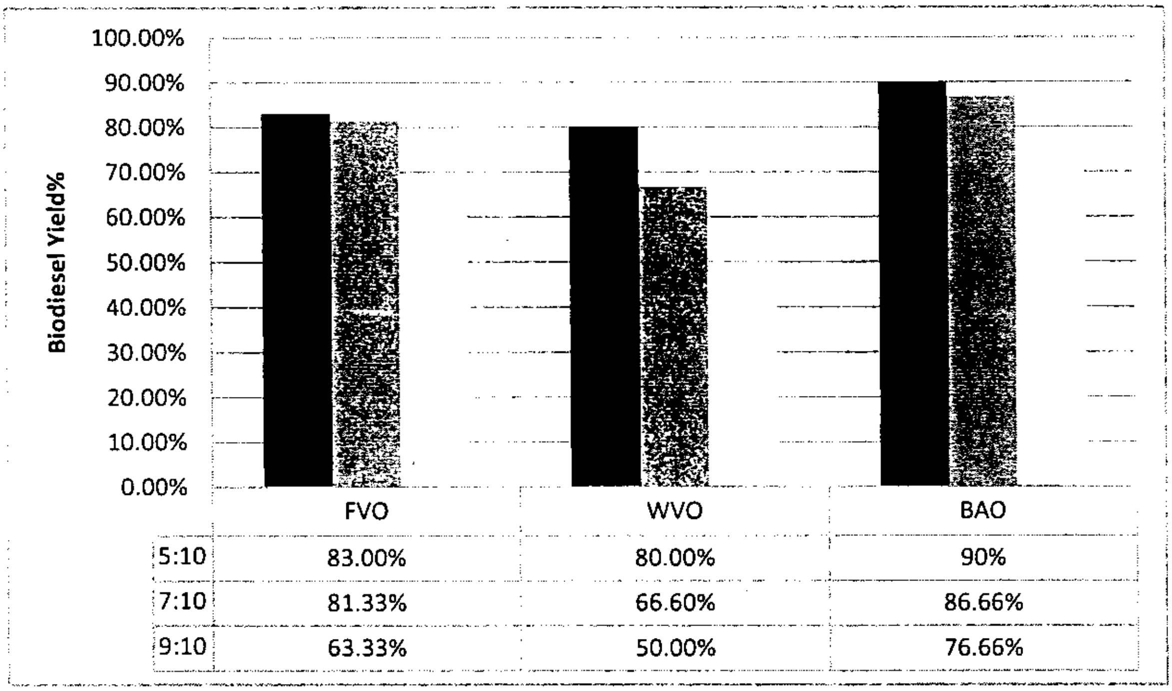
Table 4.1 Experimental Protocol for Optimization of Methoxide for Biodiesel Production

S no.	OIL SAMPLES 150ml each	RATIO	KOH BIODIESEL YIELD		NAOH BIODIESEL YIELD		KOH Glycerin by wt	NAOH Glycerin by wt
			Before wash	After wash	Before wash	After wash		
1	FVO$_A$	5:1	130ml	125ml	125ml	120ml	16.47g	20.78g
2	FVO$_B$	7:1	128ml	122ml	120ml	115ml	17.86g	18.19g
3	FVO$_C$	9:1	100ml	95ml	85ml	79ml	15.43g	14.32g
4	WVO$_A$	5:1	125ml	120ml	100ml	95ml	18.47g	31.53g
5	WVO$_B$	7:1	105ml	100ml	98ml	93ml	20.87g	32.38g
6	WVO$_C$	9:1	80ml	75ml	70ml	65ml	17.83g	28.42g
7	BAO$_A$	5:1	140ml	135ml	135ml	130ml	10.28g	12.58g
8	BAO$_B$	7:1	135ml	130ml	128ml	125ml	12.43g	16.46g
9	BAO$_C$	9:1	120ml	115ml	110ml	105ml	9.32g	10.51g

Table 4.2 Protocol for NaOH and KOH catalyst %Yield for three separate oil to methanol molar ratios for Biodiesel and Glycerin Yield

S no.	Oil samples	Oil to methanol ratio	KOH biodiesel yield%	NaOH biodiesel yield%	KOH Glycerin yield%	NaOH Glycerin yield
1	FVO$_A$	5:1	83	80	10.98	13.85
2	FVO$_B$	7:1	81.33	76.66	11.90	12.12
3	FVO$_C$	9:1	63.33	52.66	10.28	9.54
4	WVO$_A$	5:1	80	63.33	12.31	21.02
5	WVO$_B$	7:1	66.6	62.0	13.91	21.58
6	WVO$_C$	9:1	50	43.33	11.88	18.94
7	BAO$_A$	5:1	90	86.66	6.85	8.38
8	BAO$_B$	7:1	86.66	83.33	8.28	10.97
9	BAO$_C$	9:1	76.66	70	6.20	7.00

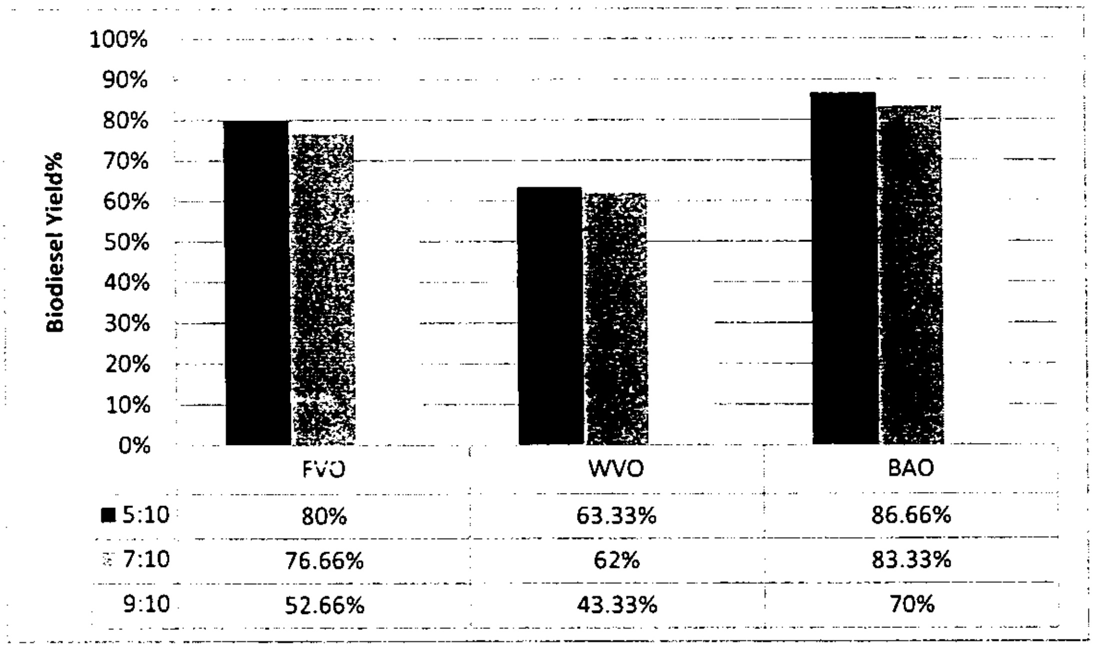
According to the results, three (3) different molar ratios of oil to methanol (5:1, 7:1 and 9:1) were optimized for the transesterification process by using 30ml, 21ml and 16ml of methanol to oil (150 ml), respectively with two different alkaline catalysts. Keeping the catalyst constant, KOH was used in concentration of 1g by wt% and NaOH of 0.9g for each sample. The volume of oil samples was 150ml for each sample thus the percentage of biodiesel produced was equivalent to the volume of biodiesel produced (Figure 4.1& 4.2).Figure 4.1 shows the effect of different oil to methanol molar ratios on biodiesel yield % with KOH concentration.



	FVO	WVO	BAO
5:10	83.00%	80.00%	90%
7:10	81.33%	66.60%	86.66%
9:10	63.33%	50.00%	76.66%

Figure 4.1Effect of oil to methanol molar ratios on biodiesel yield % with KOH

Transesterification is an equilibrium reaction in which an excess amount of alcohol is required to motivate the reaction. Therefore, the amount of MeOH was raised to optimize the biodiesel production. It was confirmed from previous studies that the concentration of reactant such as alcohol quantity result in accelerating reaction and is more advantageous to generate FAME yield (Hossain *et al*, *2009*). The results of current study confirms this explanation as the amount of MeOH increased so does the FAME yield irrespective of catalyst type (Figure 4.3 & 4.4).



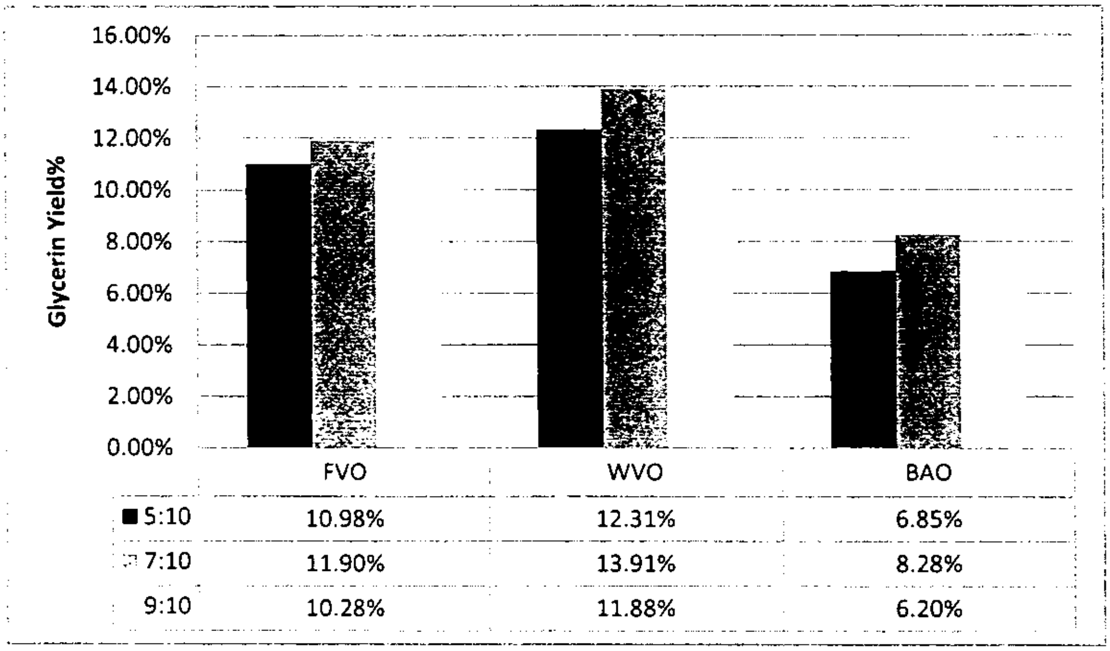
	FVO	WVO	BAO
■ 5:10	80%	63.33%	86.66%
▨ 7:10	76.66%	62%	83.33%
9:10	52.66%	43.33%	70%

Figure 4.2Effect of oil to methanol molar ratios on biodiesel yield % with NaOH

Comparison of Glycerin Yield with NaOH & KOH:

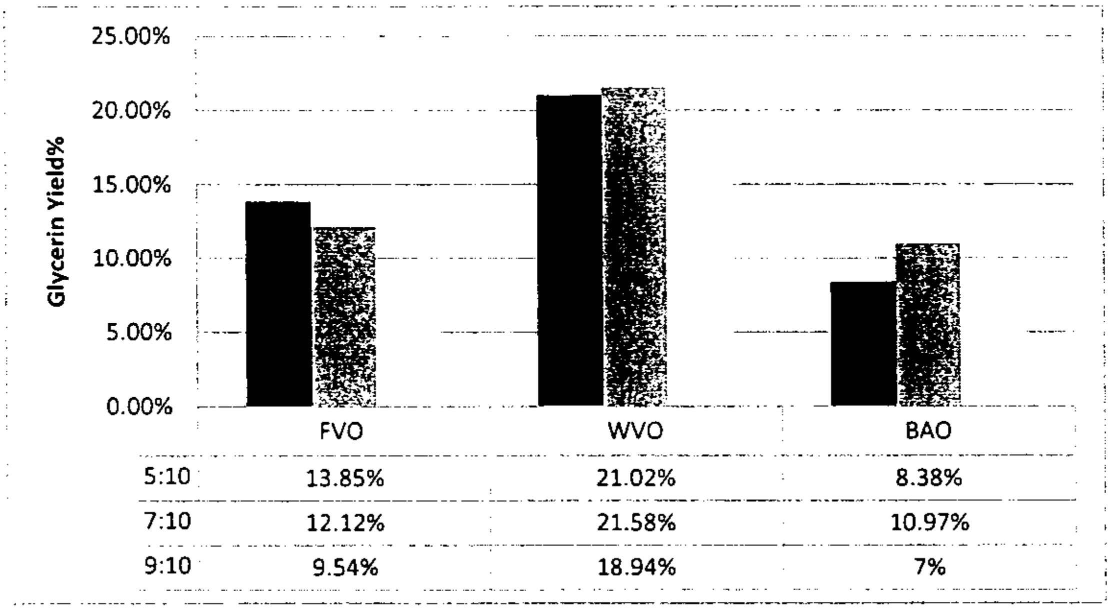
Glycerin a byproduct as a result of transesterification after separation of biodiesel was also produced with a finding that a 7:1 molar ratio liberated significantly more glycerin than did a 5:1 and 9:1 molar ratio. It was observed among all 9 samples, the highest glycerin yield for 32.38g by weight was shown by sample WVO_B optimized with 7:1 molar ratio by NaOH, whereas a molar ratio of 9:1 KOH methoxide produced lowest yield of 10.51g by sample BAO$_C$. It was found that glycerin separation was difficult in 9:1 molar ratio for all oil samples.

Singh,*et al*.,(2006) suggested that higher methanol to oil molar ratios was better than lower ratios in terms of soap formation as it increases the solubility of glycerin in biodiesel that makes the separation of biodiesel difficult and forms emulsions after wash. Furthermore, high soap formation would drive the reaction to the formation of gels, which subsequently ploys a large amount of esters within the glycerin layer and leads to the loss of biodiesel yield (Vicente *et al*., 2004). The current study was conducted at set ratio of NaOH (0.6gm é 100ml sample) and KOH (0.7gmé100ml Sample). Figures 4.3 & 4.4 show net Glycerin yield % obtained through optimization of Methanol to oil ratio with catalyst KOH and NaOH respectively. As the MeOH amount increased, glycerin production decreased. Fig 4.3 and 4.4 shows net Glycerin yield % obtained through optimization of Methanol to oil ratio with catalyst KOH and NaOH respectively.



	FVO	WVO	BAO
■ 5:10	10.98%	12.31%	6.85%
▨ 7:10	11.90%	13.91%	8.28%
9:10	10.28%	11.88%	6.20%

Fig4.3Effect of oil to methanol molar ratio on Glycerin yield % using KOH



	FVO	WVO	BAO
5:10	13.85%	21.02%	8.38%
7:10	12.12%	21.58%	10.97%
9:10	9.54%	18.94%	7%

Fig4.4Effect of oil to methanol molar ratio on Glycerin yield % using NaOH

The most significant outcome of this experiment was that a direct use of crude BAO oil as a raw material can be realized for catalyzed KOH & NaOH trans-esterification. Therefore, a higher yield of Fatty Acid Methyl Esters can be attained through crude oil transesterification in addition to simpler purification process. Among non edible vegetable oils BAO yielded highest with 5:1 molar ratio. Some good results were observed by samples 7:1 BAO_B giving yield of 83.33% and 9:1BAO_C yielding 70% of biodiesel that is more than 50% production. Many researchers believe that biodiesel yield with different oil to methanol ratio varies as the reaction is dependent on the type of feedstock used (Dorado, 2008). Among all vegetable oil samples results were above 50% as shown in table# 4.2 except 9:1WVO_C 43.33% because of its greater fatty acid content in waste oil(Hass *et al;*2001). Bitter Almond Oil all samples showed the highest yield ranging between 70-90%

either with KOH or NaOH catalysts giving the maximum yield as compared to other oil samples.

4.2 Effect of Alkaline Catalyst on Biodiesel Production:

The most frequently used method for biodiesel production is via transesterification of vegetable oil using alkaline catalysts (Singh *et al;* 2006). Biodiesel yield and oil conversion are affected by operating conditions including the catalyst formulation and its concentration. Use of alkaline catalysts can also lead to non-desirable soap formation (Arvinder *et al;* 2006). This study evaluated the alkaline catalyst effects on biodiesel yield and glycerin formation in transesterifying methanol and vegetable oils with more emphasis on Bitter Almond Oil using two different catalysts at same concentrations for all samples with varied oil to methanol molar ratios. Two different alkaline catalysts, i.e., potassium methoxide ($KOCH_3$), and sodium methoxide ($NaOCH_3$), were studied and compared on molar basis through an experimental design (Table 4.3 and 4.4).

This study compares the produce biodiesel production from Bitter Almond Oil among other oil samples by performance of both catalysts separately. The amount of KOH and NaOH, were kept constant with varied molar ratios. Reaction time was one hour and reaction temperature kept at 60-65°C throughout the experiment, near the boiling point(BP) of methanol(Zhang *et al;*2003). Methanol was optimized with KOH and NaOH to make methoxides and the effect of two individual catalysts with two different amounts was studied. KOH concentration was kept constant for all oil samples throughout the experimental work @ 5.5g/L weighing 1g and for NaOH 0.9g @ 7.5g/L for 150 ml of oil sample each.

In transesterification, the vigorous catalyst species is the methoxide radical (CH_3O-) and the activity of a catalyst depends upon the amount of methoxide radicals existing for the reaction (Komers, *et al.*, 2001). Prepared Sodium methoxide was added to preheated oil samples keeping the reaction temperature constant with constant stirring movements at 300rmp for 1hr. Table 4.1 and 4.2 shows different oil to methanol molar ratio of 5:1, 7:1 and 9:1 with constant catalyst concentration progressing biodiesel and glycerin yield%.

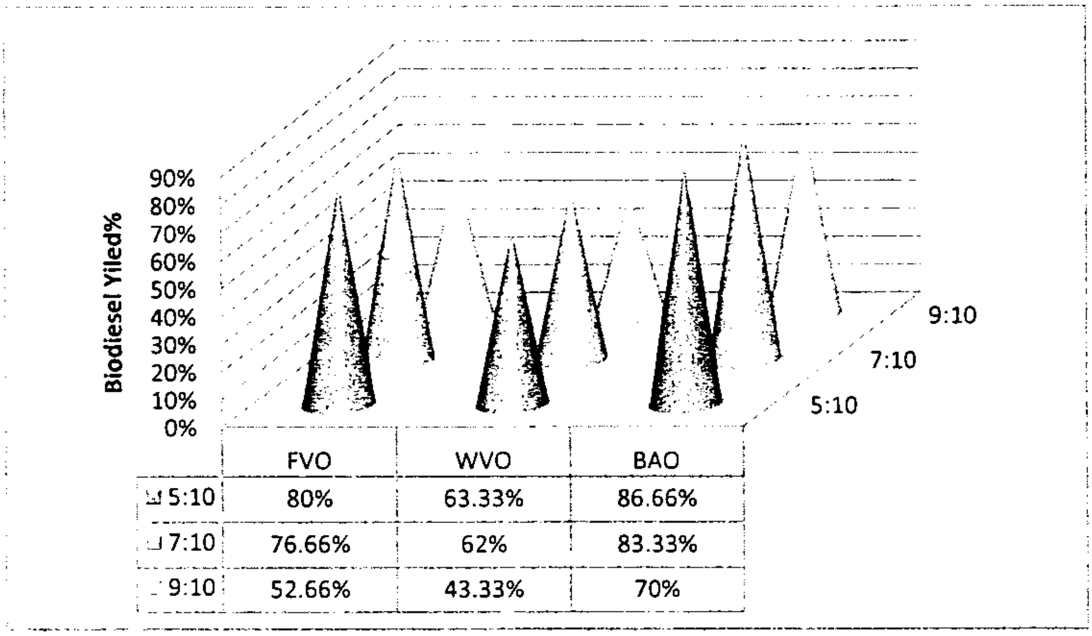
The high conversion was obtained with NaOH 0.9g to 30ml methanol ratio of 5:1 within first 20 mins, and after 1 hr FAME yield could be noticed with prominent color change and layer formation (Berchmans and Hirata, 2007) clear, golden color fluid biodiesel at the topmost and light brown glycerin at the base of container. The highest FAME yield observed was by oil samples of 5:1 molar ratio 86.66% for BAO_A, 7:1 for 83.33% of BAO_B and 9:1 for 70% for BAO_C. Minimum Glycerin (7.00%) was liberated by BAO_C of 9:1 molar ratio, 8.38% by BAO_A of 7:1 ratio and 10.97% by BAO_B of 5:1 ratio. Formation of soap was 0.0%. Lowest FAME yield was observed by samples WVO_C 43.33% of 9:1 ratio, FVO_C 52.66% of 9:1, WVO_B 62% of 7:1 and WVO_A 63.33% of 5:1 with 16ml of methanol for 9:1, 21ml for 7:1 and 30ml for 5:1 respectively. FAME yield are above 50% as it is clear in table 4.3 except 43.33% by WVO_C , because of greater free fatty acids (Freedman *et al;*2006). Maximum Glycerin yield was obtained by samples WVO_A (21.02%) and WVO_B (21.58%). It was observed that amount of Glycerin produced raised at 5:1 molar ratio and 7:1 molar ratio but dropped at 9:1 molar ratio. It was observed that rise in methanol to oil molar ratio had more outcome on the conversion to yield of biodiesel and glycerin (Zhang,*et al;* 2006).

Table 4.3 Biodiesel Production from FVO, BAO and WVO oil samples with NaOH

Oil sample	Amount of Methanol	Amount of Catalyst Sodium methoxide (gm)/ ml oil sample	Reaction Temp. (°C)	Reaction time (hr)	Biodiesel yield%	Glycerin yield%
FVO$_A$	30ml	0.9/150	60-65°C	1	80	13.85
FVO$_B$	21ml	0.9/150	60-65°C	1	76.66	12.12
FVO$_C$	16ml	0.9/150	60-65°C	1	52.66	9.54
WVO$_A$	30ml	0.9/150	60-65°C	1	63.33	21.02
WVO$_B$	21ml	0.9/150	60-65°C	1	62	21.58
WVO$_C$	16ml	0.9/150	60-65°C	1	43.33	18.94
BAO$_A$	30ml	0.9/150	60-65°C	1	86.66	8.38
BAO$_B$	21ml	0.9/150	60-65°C	1	83.33	10.97
BAO$_C$	16ml	0.9/150	60-65°C	1	70	7.00

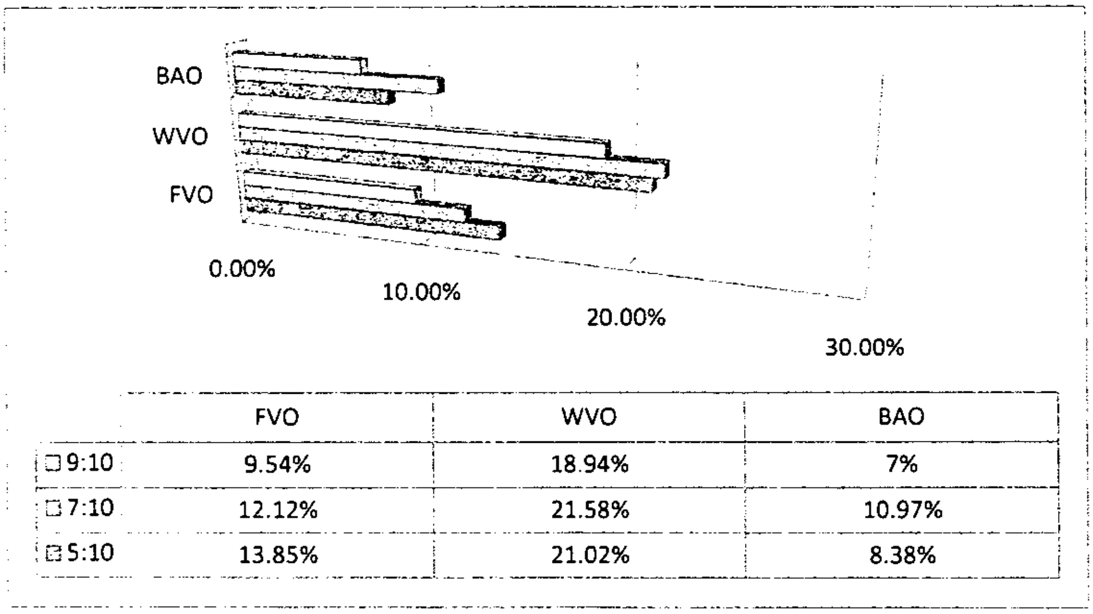
Table 4.4 Biodiesel Production from FVO, BAO and WVO oil samples with KOH

Oil samples	Amount of Methanol	Amount of Catalyst Potassium methoxide/L oil sample	Reaction Temperature	Reaction time	Biodiesel yield%	Glycerin yield%
FVO$_A$	30ml	1g/150ml	60-65°C	1 hr	83	10.98
FVO$_B$	21ml	1g/150ml	60-65°C	1 hr	81.33	11.90
FVO$_C$	16ml	1g/150ml	60-65°C	1 hr	63.33	10.28
WVO$_A$	30ml	1g/150ml	60-65°C	1 hr	80	12.31
WVO$_B$	21ml	1g/150ml	60-65°C	1 hr	66.6	13.91
WVO$_C$	16ml	1g/150ml	60-65°C	1 hr	50	11.88
BAO$_A$	30ml	1g/150ml	60-65°C	1 hr	90	6.85
BAO$_B$	21ml	1g/150ml	60-65°C	1 hr	86.66	8.28
BAO$_C$	16ml	1g/150ml	60-65°C	1 hr	76.66	6.20



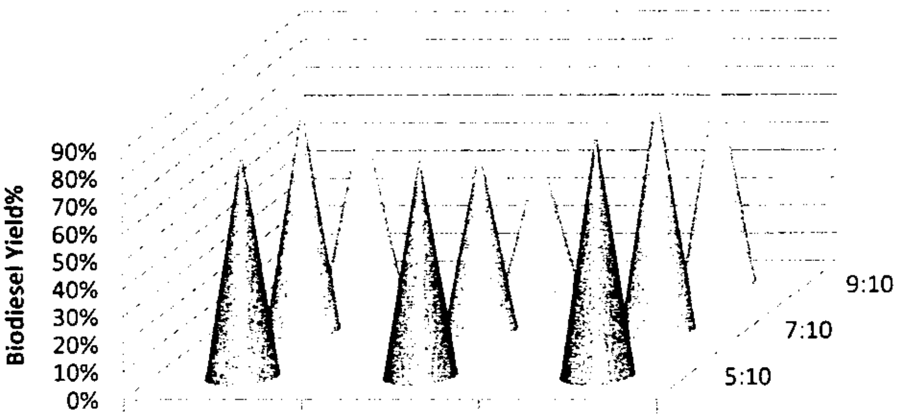
	FVO	WVO	BAO
5:10	80%	63.33%	86.66%
7:10	76.66%	62%	83.33%
9:10	52.66%	43.33%	70%

Fig 4.5 Biodiesel yield% with different methanol ratios using NaOH



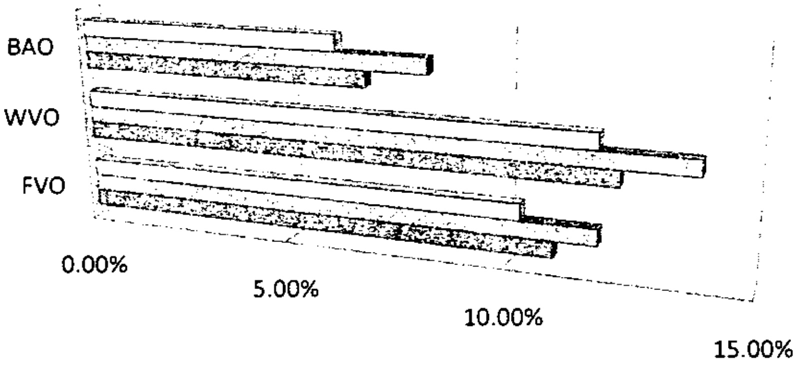
	FVO	WVO	BAO
9:10	9.54%	18.94%	7%
7:10	12.12%	21.58%	10.97%
5:10	13.85%	21.02%	8.38%

Fig 4.6 Optimum Glycerin yield% with different methanol ratios using NaOH



	FVO	WVO	BAO
5:10	83%	80%	90%
7:10	81.33%	66.60%	86.66%
9:10	63.33%	50%	76.66%

Fig 4.7 Optimum Biodiesel yield% with different methanol ratios using KOH



	FVO	WVO	BAO
☐ 9:10	10.28%	11.88%	6.20%
☐ 7:10	11.90%	13.91%	8.28%
☐ 5:10	10.98%	12.31%	6.85%

Fig 4.8 Optimum Glycerin yield% with different methanol ratios using KOH

The high conversion was obtained with KOH1g to30ml methanol ratio of 5:1 molar ratio. The highest FAME yield observed was by oil samples of 5:1 molar ratio 90% for BAO_A, 7:1 for 86.66% of BAO_B and 9:1 for 76.66% for BAO_C. Minimum Glycerin(6.2%) was liberated by BAO_C of 9:1 molar ratio, 8.25% by BAO_B of 7:1 ratio and 6.85% by BAO_A of 5:1 ratio. Formation of soap was 0.0%. Lowest FAME yield was observed by samples WVO_C 50 % of 9:1 ratio, FVOC 63.33% of 9:1, WVOB 66.6% of 7:1 with 16ml of methanol for 9:1, 21ml for 7:1 and 30ml respectively. However a good yield by WVO_A80% by KOH of 5:1 was observed as compared to NaOH results for WVO_A (63.33%). Secondly FAME yield is not below than 50% as compared to NaOH reaction by sample 9:1 (43.33%). Maximum Glycerin yield was obtained by samples WVO_A(12.31%) and WVO_B (13.91%). Glycerin yield was quite low in reactions with KOH ranging between 6.2%-13.91% maximum. Lowest glycerin liberated was by BAO_C(6.2%). Table 4.4 shows that this percentage is significantly low as compare to reactions with NaOH as a catalyst.

It was observed that potassium methoxide led to better biodiesel yields than sodium methoxide catalyst. The methoxide catalysts not only accelerated the reaction but also elevated the conversion equilibrium (Thompson *et al;*2006). Based on statistical optimization, the operating conditions for maximizing biodiesel yield and minimizing Glycerin formation were potassium methoxide as catalyst at 5:1, 7:1 and 9:1mol/mol (0.1%wt) and reaction temperature of 60°C, and methanol-to-oil molar ratio of 5:1 by Bitter Almond Oil sample producing experimental verification of 90% wt biodiesel yield and 6.85% wt glycerin proving$KOCH_3$>$NaOCH_3$.

This catalyzed method of transesterification is new efficient& effective process, therefore offers a modest technology for generating an alternative fuel for diesel engines with a potentially low cost. The environment friendly renewable resource and biotechnologically developed method renders considerable yield of Fatty acid Methyl Esters preferably appropriate for application in industry. However, the rate of conversion rises with growing molar ratios (Atapoura and Karminia, 2010).

4.3 Physico-chemical characterization of BAO biodiesel

In the present research project pure plant seed oil BAO was optimized to three ratios to produce a renewable biodiesel resource and was studied for physico-chemical properties. The result of biodiesel properties was similar to ASTM (American Standard& Material testing) standard as shown in Table 4.5.

During the process of transesterification, transitional product that is glycerol, mono and diacylglycerols may be produced, which can persist in minor amounts ultimately in the biodiesel. Besides this unreacted triacylglycerol's, fractional glycerol's, non-separated glycerol, FFA'S, and alcohol left can impure the absolute product. These impurities can give rise to certain operational complications while consuming biodiesel, such as filter clogging, engine deposits, and therefore the ASTM (American Standard & Material Testing) method is followed.

Table 4.5 Fuel properties of Biodiesel Specification for (B100)-ASTM D6751-07a

Fuel properties	**Method**	**Limits**	**Units**	**BAO_A B100(5:1) KOH**	**BAO_B B100(7:1) KOH**	**BAO_C B100(9:1) KOH**	**Petro-diesel[1]**
Flash Point (PMCC)	D-93	130min	°C	193	188	191	85
CloudPoint	D-2500	min-15 max -5	°C	-4	-6	-9	-19
Pour Point	D-97	min-35 max-10	°C	-8	10	-3	-23
Kinematic Viscosity @ 40 °C	D-445	1.9 to 6	mm^2/sec	2.56	4.67	4.8	2.39
Density@ 15 °CKg/L	D-1298	0.8343	g/cm^3	0.862	0.888	0.8224	0.847 (25°C)
Sulphur % wt	D-4294	0.05	%masspppm	0.042	0.03	0.028	0.05
Specific gravity	---	0.851	---	0.887	0.840	0.792	0.88
Cetane Number	D-613	47min	---	43.82	45.21	44.5	46
Total Acid mg KOH/gm	D-974	0.50 max	MgKOH/g	0.34	0.25	0.49	NA
Color	D-1500	---	---	1.5	2	1.0	2
Iodine Value	EN14214	120max	mg/I_2/g	117.29	112.32	118.74	NA

For the current study, the value of the density @15°C kg/h of BAO B100 with BAO_A (0.862), BAO_B (0.888) and BAO_C(0.8224) was recorded. The value of the densities in the present analysis was quite comparable to those reported in the literature (Atapour,*et al*; 2010 and Encinar, *et al;* 2005). The ASTM standard D-445 prescribed the kinematic viscosity @ 40°C cSt ofB100 BAO_A (2.56), BAO_B(4.67) and BAO_C(4.8) which is within biodiesel standard as mentioned in table 4.3.1 and quite comparable to Petro-diesel(2.39). The other fuel properties like color comparison studied in BAO_A. BAO_B and BAO_C showed similar behavior and meet the international biodiesel and petro-diesel standard. Cetane number is slightly lower than the standard limit that is 43.82 for BAO_A and 45.21, 44.5 for BAO_B and BAO_C respectively.

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[1] Encinar*etal;* (2005).

The maximum values of cloud and pour points of biodiesel in all three samples of BAO in the present work were also in accordance with ASTM standard. The flash point °C of BAO biodiesel was (BAO_A: 193, BAO_B: 188, BAO_C: 191) met the ASTM standard of D93 >130 and in contrast the flash point of petro-diesel was 60-85. The flash point of BAO_A, BAO_B, BAO_C biodiesel were higher than petro-diesel. Flash point is the main parameter of biodiesel in safety, storage and flammable material. As the high flash point reduces the risk of fire the parameter were also similar to the biodiesel properties as studied by other people (Umer & Anwer, 2008).

Iodine value is also an indicator of stability, whereby a high iodine value is related to the point of polymerization, which may lead to injector fouling in engine (Thyssen, 2008). Iodine value for BAO_A: (117.29), BAO_B: (12.32) and BAO_C: (118.74) were within standard limit of Iodine specification EN14214. Biodiesels with low iodine values have relatively low levels of unsaturation and are less subtle to oxidation processes. Since biodiesel is biodegradable in nature, hence less in stability as compared to petro-diesel(Anonymous, 2006).

ASTM D-4294, D-975, analyzed the sulfur contents of BAO biodiesel. The value of sulfur contents of Bitter Almond Oil were (BAO_A: 0.042, BAO_B: 0.03, BAO_C: 0.028). In petro-diesel the value of sulfur was 0.05. Various oxides of sulfur are too toxic to environment and in biodiesel the value of sulfur is negligible, that is why biodiesel are considered as environment friendly.

4.4 FT-IR analysis of BAO VS Other Oils

Production of biodiesel was carried out from crude oil of Bitter Almond BAO and other two samples from straight and waste vegetable oils. Biodiesel was chemically characterized with FT-IR to analyze the chemical composition of BAO biodiesel in comparison with other vegetable oils. Infrared Spectroscopy is used in the monitoring of transesterification reaction (Knott, 1999). Table of Infrared Absorption Frequencies can be seen in annexure. Infra-red study of BAO shows bending and stretching vibrations indicating presence of methyl ester functional groups(C–H, C=O, C=C and C–O) different bonds having different vibrational frequencies. Four samples of BAO and three samples each for FVO and WVO were scanned from the wavenumbers for absorption bands in mid IR range of 4000 cm^{-1} to 450 cm^{-1}.

The BAO samples with various Oil to MeOH ratio were analyzed by infrared spectrometry in comparison with other vegetable oil samples WVO and FVO and their spectra were studied at three different spectral ranges: full spectrum (4000 to 450cm^{-1}),2927-2856cm^{-1}, and the spectral ranges of 1744-1747 cm^{-1} and 1462-1362 cm^{-1}.

Ten (10) biodiesel samples were analyzed for FTIR analysis. Sample 1, 2, 3 and 4, corresponding to BAO in Table 4.6 shows the normalized FTIR spectra obtained for the four different Biodiesel fractions from the esterified product of the BAO. Each spectrum was normalized by the intensity of the absorption band centered at 2930 cm^{-1} (the strongest band). Among four BAO samples a characteristic vibrational mode was observed at 3009 cm^{-1} (CH stretching, Olefinic) by sample 2 and (CH stretching, aliphatic) 2850–

2980 $cm^{-1}$by sample1, 2 and 3 while sample 4 was featured by 2856.53cm^{-1} absorption frequency of BAO proved the presence of carboxylic acid. C=O stretching of methyl group esters 1740 to1747 cm^{-1} by all ten sample indicated esters in samples, a sharp trend being observed by sample 1,2,3 and 4 of BAO as compared to sample 5 and 6 of FVO and sample 10 of WVO that showed rather broad stretched absorption band. A small but pointed stretch at 1652 cm^{-1} (C=C stretching, Olefinc) indicated Arenes group of unsaturated esters in all samples ranging between 1654-1655cm^{-1} for BAO samples. Feature of C=C stretching was also observed in other investigated samples except sample 9 of FVO where it was indication of C=C group but peak was not observed, the reason for which is not known (Table 4.6).

The application of spectroscopic technique for assessment of biodiesel quality and monitoring, among each has significant inspected complications. Biodiesel can origin dilution, ultimately leading to engine failure (Sadeghi-Jorabchi,*et al*; 1994). As compared to conventional diesel fuel the dilution remained accredited to the most likely upper boiling range of biodiesel. However, no method can alone satisfy all the parameters of chemical composition due to trifling speculation of cost, labor and time. The followed applied methodology such as Infrared Spectroscopy is therefore reasonable and reliable which are too fast and easy to use and to adopt for the production of biodiesel monitoring.

Table 4.6 FTIR absorption frequencies of Biodiesel from Oil Samples with respective Functional group

Sample No	Oil Samples	C−H group	C=O group	C=C group	C−O group
1	BAO	2927.92-2856.42	1744.94	1644.82	1462.14
2	BAO	2928.03-2858.89	1745.00	1655.94	1462.67
3	BAO	2927.92-2856.42	1744.94	1654.82	1462.14
4	BAO	2856.53	1745.06	1655.29	1462.95
5	FVO	2923.38	1741.05	1656.17	1448.69
6	FVO	2923.17	1739.03	1655.92	1449.00
7	FVO	2919.37	1742.50	1655.47	1452.39
8	WVO	2865.96	1744.50	1554.92	1458.29
9	WVO	2927.86-2856.68	1744.73	1666.02	1464.39-1436.77
10	WVO	2922.61	1740.01	1655.79	1451.40

4.5 Review of analysis of Fatty Acid Methyl Esters FAME by GC-MS

The Iranian bitter almond oil's characterization confirmed that its physicochemical properties are parallel to that of some of the vegetable oils. The acid value of the Bitter Almond Oilstood0.24 mg KOH/g, which indicated that it was not obligatory to undergo the process for pre-treatment of crude oil with acid. Atapoura, *et al*,, (2010) quantify and composition the methyl ester in BAO biodiesel & was determined by using a HP 6890 series 2 gas chromatograph with a flame ionization detector according to biodiesel test method UNE-EN 14103.DB-WAXwas the capillary column with30 m of length ,0.32 mm an internal diameter&0.25 lm a film thickness . Helium was used as an auxiliary gas& also as a carrier gas for the Flame Ionization Detector. One µl of sample using a 6890 Agilent Series Injector was injected.

The contribution of unsaturated fatty acid composition analysis indicated that acids in the BAO existed 84.7 wt.% comprising Oleic acid(33.9%), Linoleic acid(46.0%) and 4.8% of Linolenic acid. Total FFA mainly comprises stearic acid & Palmitic acid is the saturated fatty acids consisting of 14.5%. Determination of the rest of the fatty acid composition (0.8%) that included small amounts of other components was not observed. The reduced cloud point& cetane number could be due to high content of unsaturated fatty acids whereas reduced stability of formed biodiesel due to the increased extent of unsaturated FAME (Ramadhas,*et al*; 2005).

Table 4.3 and Appendix 6 show physico chemical properties of biodiesel and properties of Almond oil respectively. It is concluded from table that except cetane number, all the properties of BAO biodiesel, counterfeit to standards of EN 14214 and ASTM 6751, though lower cetane number than the limits standardized as discussed earlier in chapter 4.3. Due to fatty acid composition of the BAO (obtained through a reference) in appendix 6, rational value of cetane number is observed, consisted mostly Palmitic acid (10.3 wt. %), Oleic acid (33.9 wt. %) and Linoleic acid by 46.0 wt. %. The cetane numbers of Methyl Palmitate (85.9), Methyl Oleate (59.3) and Methyl Linoleate (38.2) and reason for reduced cetane number is the high unsaturated fatty acids content that is 84.7% wt.

It is concluded based on the results that BAO possess the potential to become a substrate for Biodiesel production due to its Physico-chemical characteristics and Fatty acids profile. Further studies are in progress to evaluate its pure (B100) and different combination of Biodiesel with petro-diesel, in order to optimize engine performance and eventually the emissions.

V. CONCLUSION AND RECOMMENDATION

The accessibility of regenerated reserves of fossil fuel and contemporary environmental problems triggered by the consumption of fossil fuels has drawn substantial thoughtfulness to an alternative source replacing petro-diesel for biodiesel production. However, as the biodiesel can be produced from vegetable oils but the concern arises that biodiesel feedstock may contest with edible stock, especially in developing countries. Hence, the recently motivation is required to sort tree-bearing oils (TBO) that yield non-edible oils as the feedstock for production of biodiesel. In this research *prunusamygdalus* bitter almond variety among Fresh and Waste vegetable oil samples were conferred as innovative sources of oil for production of biodiesel and its physic-chemical properties was discussed in detail under ASTM and EN14214 standards. After experimental analysis it was verified that oil as feedstock has a great probability to be used for biodiesel making, producing 45-50% fixed oil from seeds, 30% oil after treatment from kernels and 1% from powdered cake of Bitter Almonds after macerated with water. Together it could contribute to more than 75% oil if feedstock being utilized as biofuel energy resource.

FTIR analysis of BAO was done for the first time in this study and it concluded the significant property of biodiesel exhibiting methyl group esters and other Arenes group showed sharper peaks as compared to other vegetable oil samples in which ester group were present and showed rather broader and blunt peaks.

The physico chemical properties of BAO are parallel to that of some other oil bearing plants being utilized for biodiesel production which was confirmed by characterization of the bitter almond oil obtained from Northern areas. The pretreatment of crude oil with acid was not requisite because of the acid value of the BAO which was 0.24 mg KOH/g. The FAME composition of the Bitter Almond Oil from reference proved that the amount of unsaturated fatty acids in the BAO was high (84.7 wt. %). The BAO was transesterified consuming methanol with Sodium hydroxide & Potassium hydroxide for biodiesel production. Optimum parameters including effect of methanol to oil molar ratios, effect of Potassium hydroxide and Sodium hydroxide concentration, reaction time and reaction temperature on yield of Biodiesel and Glycerin were observed. According to the results the studied parameters were imperative factors that affected the transesterification reaction of the oil samples. An elevation in biodiesel yield (90 wt. %) was attained with a low Glycerin production (6.85 wt.%) by $KOCH_3$ as compared to(86.66%wt)Biodiesel and Glycerin yield(8.38%wt) by $NaOCH_3$ at methanol to oil molar ratio of 5:1 mol/mol with potassium hydroxide concentration of 1g w/w and Sodium hydroxide of 0.9gw/w with temperature maintained at 60-65°C. This proves that potassium methoxide produced the highest yield of BAO biodiesel with minimum side product glycerin generation hence verifying $KOCH_3 > NaOCH_3$. According to standards of EN 14214 and ASTM 6751 the figured properties of the biodiesel imitated, except cetane number. By blending it with petro-diesel the matter of low cetane number of the produced biodiesel can be resolved.

Bitter almond is found abundantly in Mediterranean climatic areas of Pakistan, widely adulterated with sweet almonds in order to meet high demands of edible sweet variety. Although much of the attention has been given to the use of nonedible oil bearing seeds for biodiesel production but no decisive step has been taken for use of such alternative crops which require least maintenance cost like bitter almond plant at commercial scale.

Biofuel derived from non-edible oil bearing seeds have progressed from being virtuously investigational fuels to early stages of commercialization. These non-edible seed sources for biodiesel are precisely economical with or propose more methodological advantages in comparison to conventional diesel fuel. Moreover being a renewable, biodiesel reduces most emissions and is a domestic resource, while fuel economy& engine performance are closely corresponding as compared to conventional fuels. However, several complications remain including combustion, economics, some other emissions, lube oil adulteration, and reduced-temperature properties. Financial motives have been one of the main obstacles in the usage of biodiesel which mainly inculcates the cost of feedstock for biodiesel production. Operating cost of biodiesel plant in Pakistan isapprox.85% of the total to acquire feedstock. Critical factors in controlling profitability is sourcing it locally to avoid long shipping for delivery of the seeds to biodiesel plant, hence acquiring own feedstock would insure supply at a fair price . This could only be possible at commercial scale if our own harvesting lands are cropped for certain feedstock.

- The villagers could grow the required feedstock for the non-edible fuel resource like Bitter Almond and can produce Biodiesel through trans-esterification and run the installed generator set to generate electricity for their village.
- Pakistan being an agriculture-based economy can produce Biodiesel from non-food crops. This will fortify Pakistan's agricultural region and endow the farmers.

- Money does not grow on trees, but trees like TBO could be a possible energy solution. Production of TBO like Bitter almonds in the proposed study could be used to yield biofuel at commercial scale utilizing its wild variety from vast waste lands in Northern areas and west Baluchistan.
- Besides these plants have the potential to nurture on waste or arid marginal land, a huge area of such poor quality land (more than 80 million acres) is ideal for the propagation of such energy crops in Pakistan. Fostering Bitter Almonds would not dissuade land away from budding vital food crops.
- The total impact on agricultural occupation alone could be huge by plantation of these plants hence likely for every acre of planted trees creating at least one job.
- Besides vegetable oil, alcohol (methanol) is like wise required to produce biodiesel. Only about 10% of the volume of biodiesel is constituted by alcohol. Methanol can be conveniently obtained from natural gas.

In a nutshell land is available, technology is accessible other essential raw materials are indigenous and can be obtained from wastelands; the only thing needed is the will to do it and thinkable use of cost effective nonfood crops for fuel. For the supply of second-generation biofuels there is also a dire necessity of a step headed for large-scale production and that is oil from plant seeds, although in preliminary platform, to fortify the world economy in general and Pakistan's in particular. However, the generation of biofuels like biodiesel is likely to have thoughtful socio-economic implications specifically to the lesser developed society's dependent on oil imports from foreign countries. This needs serious consideration from policy makers and general masses at large.

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APPENDICES

APPENDIX 1

Pictures of Almond Plant and its Seeds

Bitter Almond

Short and broad structured

Sweet Almond

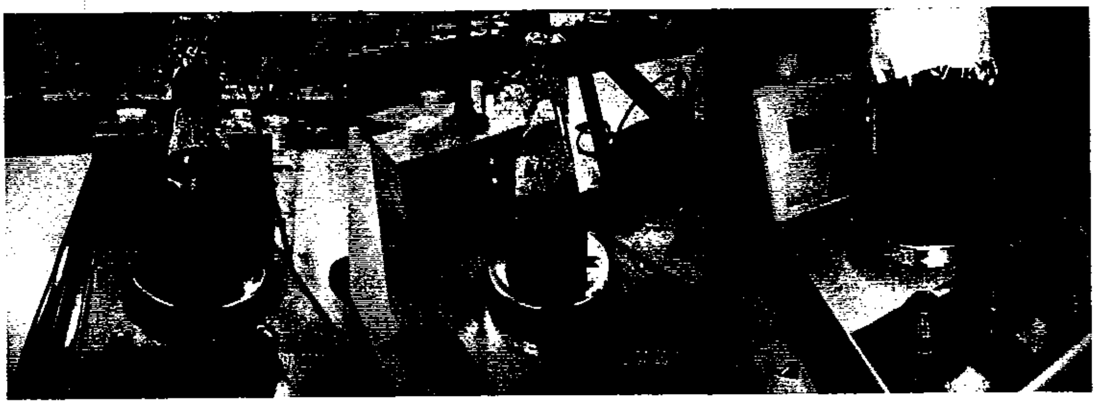
Long and sleek Structured

Bitter Almond Pink Flowers

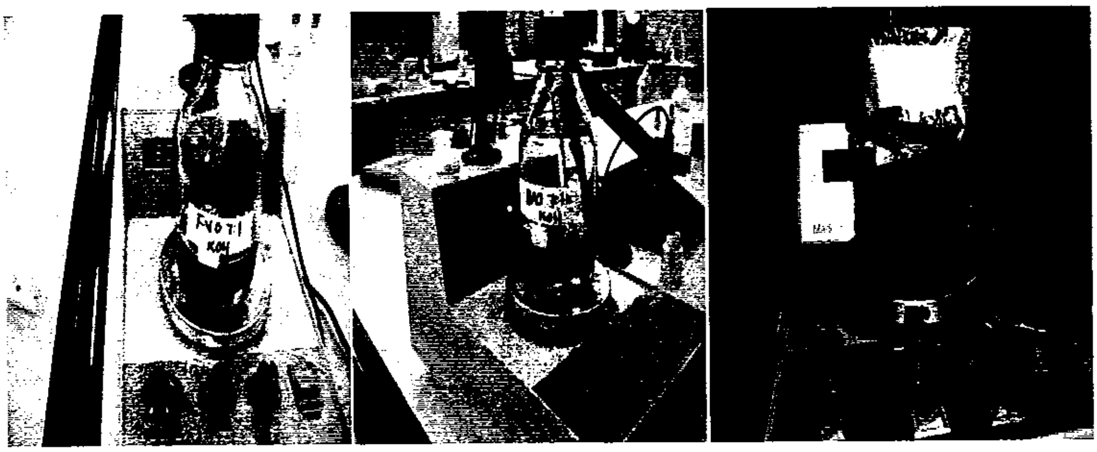
Sweet Almond White Flowers

APPENDIX 2: Synthesis of Biodiesel

I. Synthesis of Biodiesel from BAO,FVO & WVO Oil samples(5:1) ratio KOH



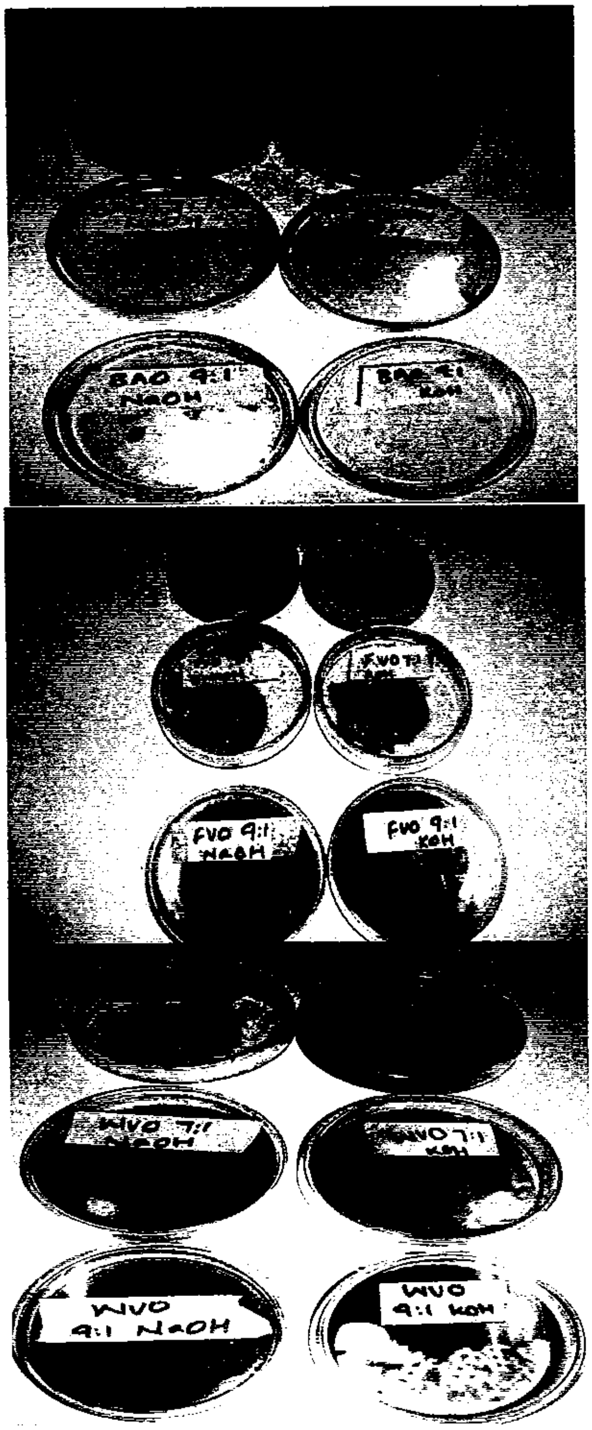
II. Synthesis of Biodiesel from BAO, FVO & WVO Oil samples (7:1) ratio KOH



III. Synthesis of Biodiesel from BAO, FVO & WVO Oil samples (9:1) ratio KOH

APPENDIX 3

Glycerin yield from BAO, FVO & WVO Oil samples optimizing 5:1, 7:1 and 9:1 ratiofor NaOH and KOH



APPENDIX 4

Infrared Absorption Frequencies for Oil

	Stretching Vibrations			Bending Vibrations		
Functional Class	**Range (cm^{-1})**	**Intensity**	**Assignment**	**Range (cm^{-1})**	**Intensity**	**Assignment**
Alkanes	2850-3000	str	CH_3, CH_2 & CH 2 or 3 bands	1350-1470 1370-1390 720-725	med med wk	CH_2 & CH_3 deformation CH_3 deformation CH_2 rocking
Alkenes	3020-3100 1630-1680 1900-2000	med var str	=C-H & =CH_2 (usually sharp) C=C (symmetry reduces intensity) C=C asymmetric stretch	880-995 780-850 675-730	str med med	=C-H & =CH_2 (out-of-plane bending) cis-RCH=CHR
Alkynes	3300 2100-2250	str var	C-H (usually sharp) C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
Arenes	3030 1600 & 1500	var med-wk	C-H (may be several bands) C=C (in ring) (2 bands) (3 if conjugated)	690-900	str-med	C-H bending & ring puckering
Alcohols & Phenols	3580-3650 3200-3550 970-1250	var str str	O-H (free), usually sharp O-H (H-bonded), usually broad C-O	1330-1430 650-770	med var-wk	O-H bending (in-plane) O-H bend (out-of-plane)
Amines	3400-3500 (dil. soln.) 3300-3400 (dil. soln.) 1000-1250	wk wk med	N-H (1°-amines), 2 bands N-H (2°-amines) C-N	1550-1650 660-900	med-str var	NH_2 scissoring (1°-amines) NH_2 & N-H wagging (shifts on H-bonding)
Aldehydes & Ketones	2690-2840(2 bands) 1720-1740 1710-1720	med str str str	C-H (aldehyde C-H) C=O (saturated aldehyde) C=O (saturated ketone)	1350-1360 1400-1450	str str med	α-CH_3 bending α-CH_2 bending

	1690	str		1100		C-C-C bending
	1675	str	aryl ketone			
	1745	str	α, β-unsaturation			
	1780		cyclopentanone			
			cyclobutanone			
Carboxylic Acids &Derivativs	2500-3300 (acids)	str	O-H (very broad)	1395-1440	med	C-O-H bending
	overlap C-H	str	C=O (H-bonded)			
	1705-1720 (acids)	med-str	O-C (sometimes 2-peaks)			
	1210-1320 (acids)					
		str				
	1785-1815 (acyl halides)	str	C=O			
		str	C=O (2-bands)			
		str	O-C			
	1750 & 1820 (anhydrides)	str	C=O		med	
		str	O-C (2-bands)	1590-1650	med	N-H (1°-amide) II band
	1040-1100		C=O (amide I band)	1500-1560		N-H (2°-amide) II band
	1735-1750 (esters)					
	1000-1300					
	1630-1695(amides)					
Nitriles	2240-2260	med	C≡N (sharp)			
Isocyanates,Isothiocyanates, Diimides, Azides& Ketenes	2100-2270	med	-N=C=O, -N=C=S -N=C=N-, -N_3, C=C=O			

APPENDIX 5

Determination of FFA through aqueous acid base Titration

APPENDIX 6

Properties of BAO

Properties	**Nomenclature**	**Bitter Almond Oil**
Saturated Fatty Acids composition(wt%)		
Myristic Acid	C 14 : 0	0.1
Palmitic Acid	C 16 :0	10.3
Stearic Acid	C 18:0	3.9
Arachidic Acid	C 20:0	0.2
Unsaturated Fatty Acids composition(wt%)		
Oleic Acid	C 18:1	33.9
Linoleic Acid	C 18:2	46
Linolenic Acid	C 18:3	4.8
Total molecular weight MW g/mol		866

Fatty acid composition of Bitter almond Oil BAO by GC-MC analysis[2]

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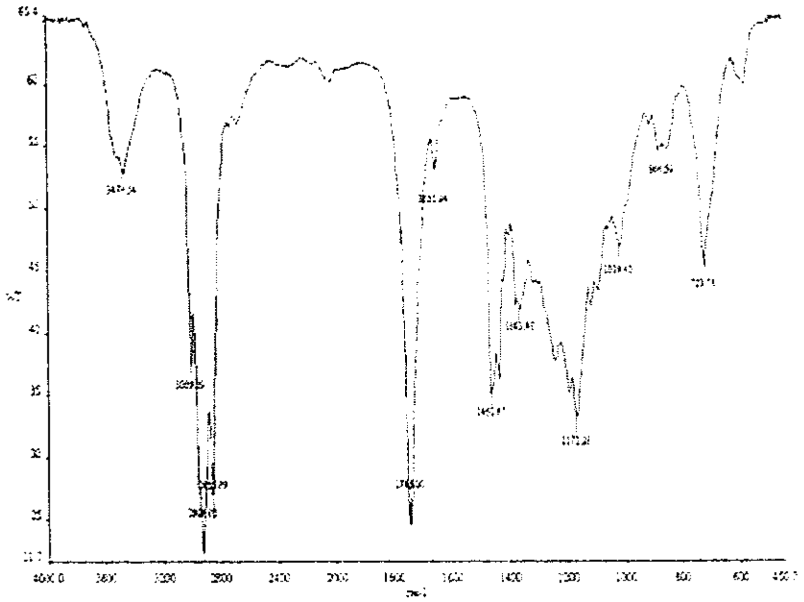
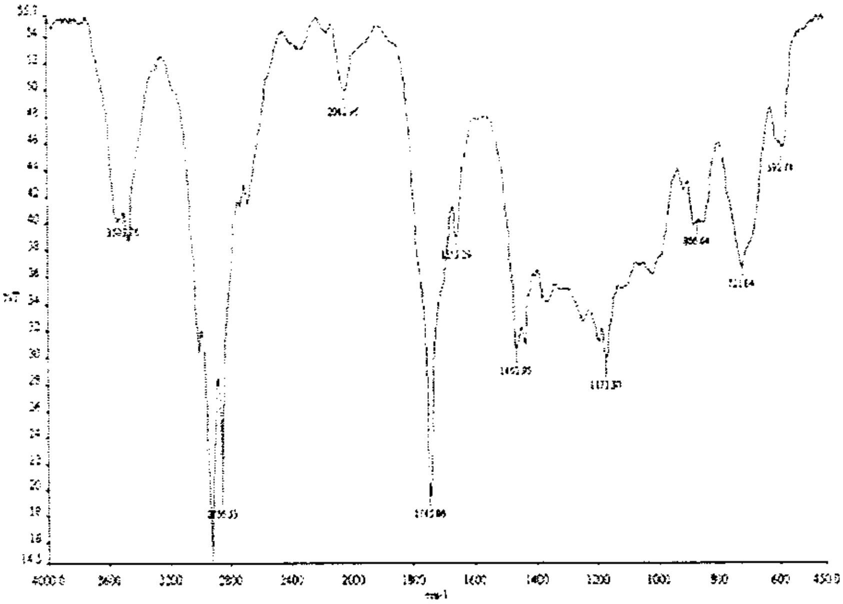
[2] Knothe G;(2003)

APPENDIX 7

FTIR Analysis for Biodiesel Samples

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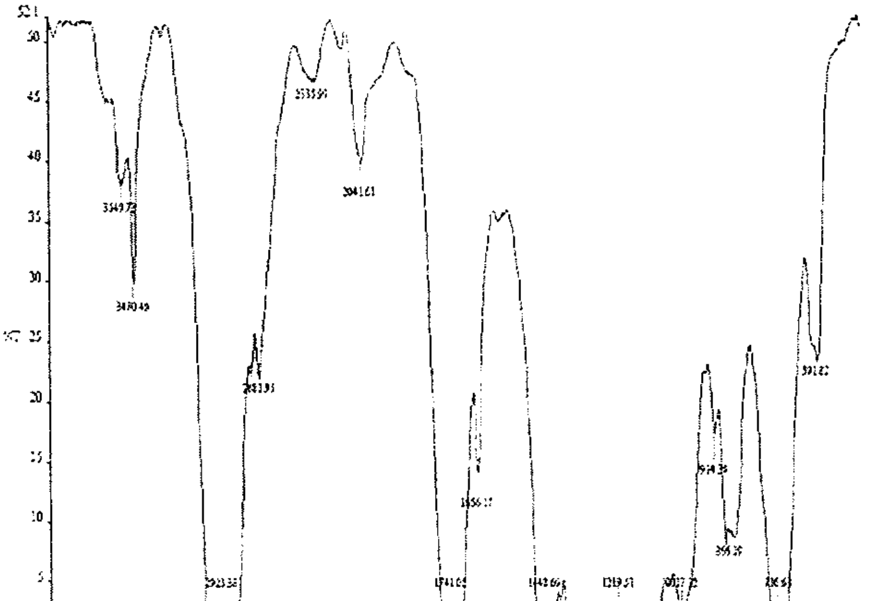
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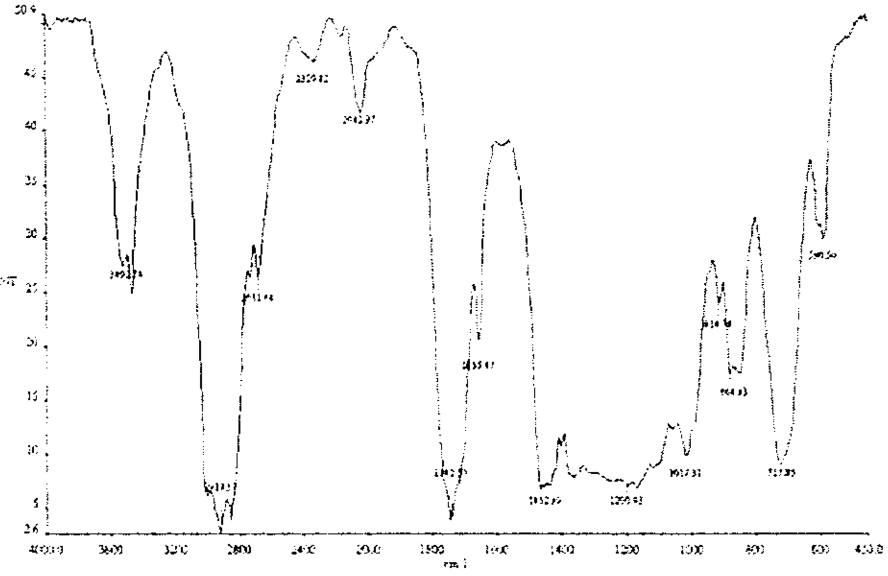
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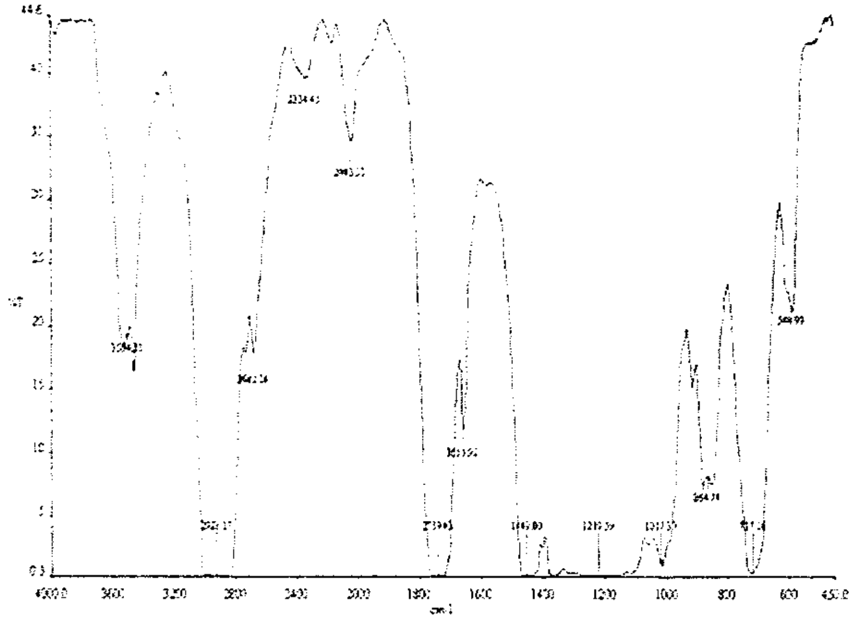
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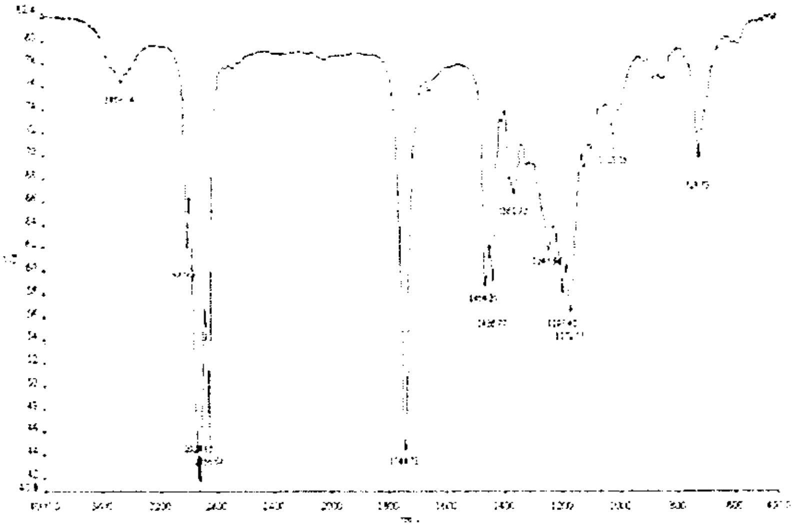
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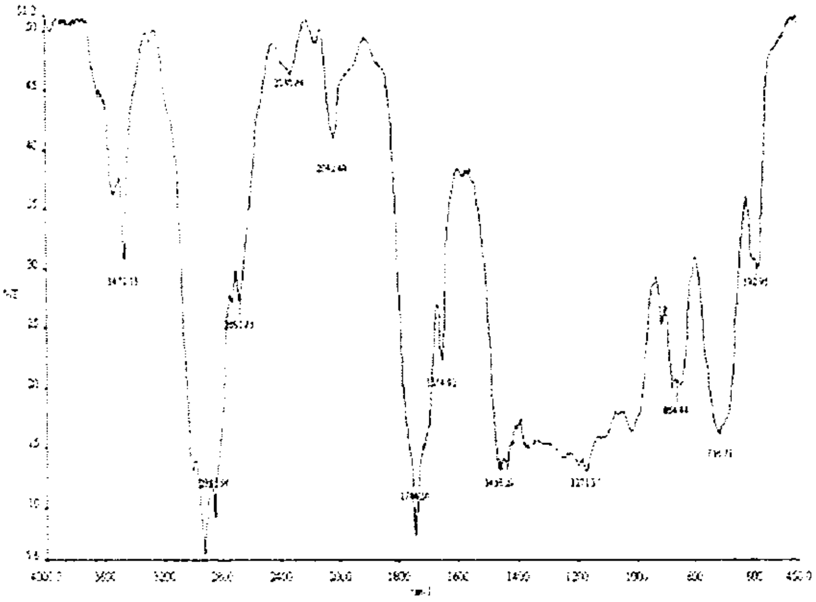
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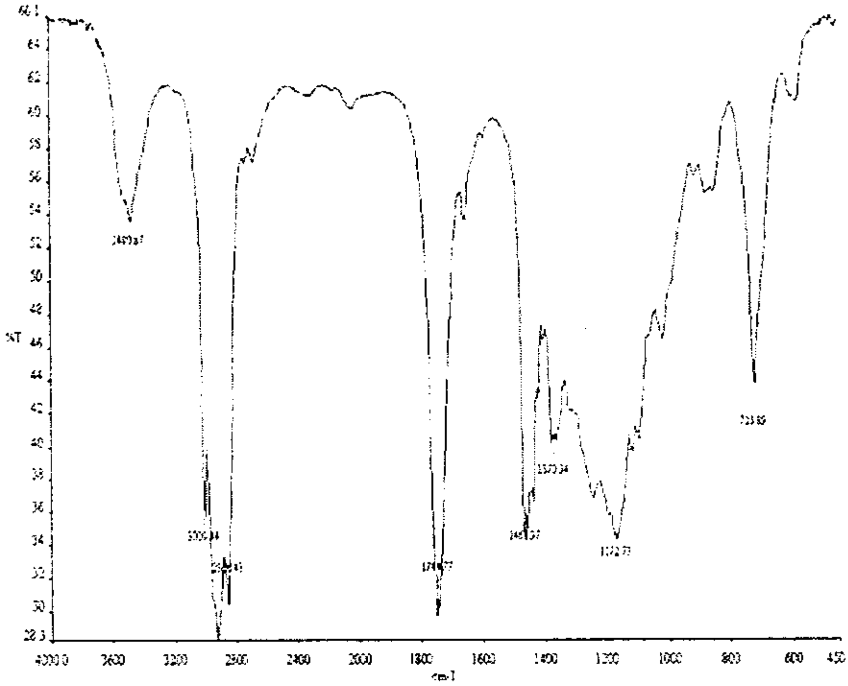
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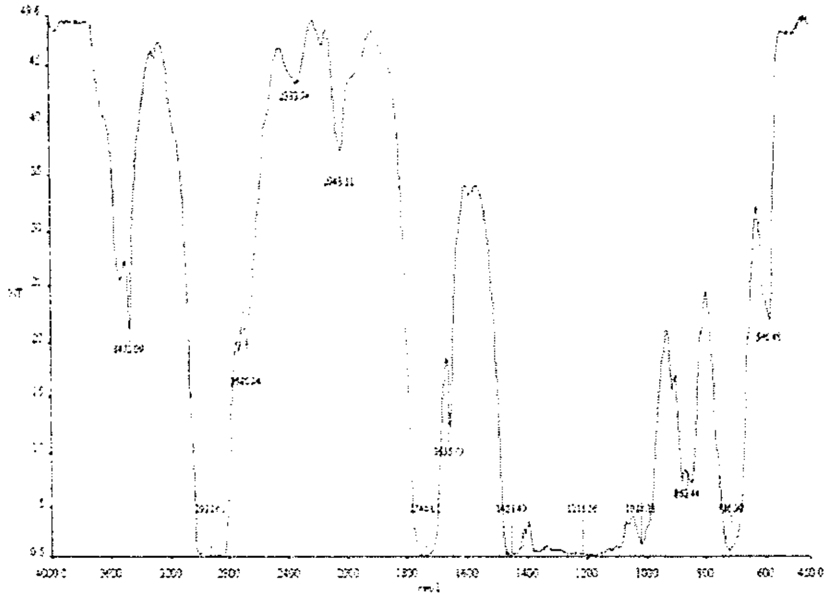
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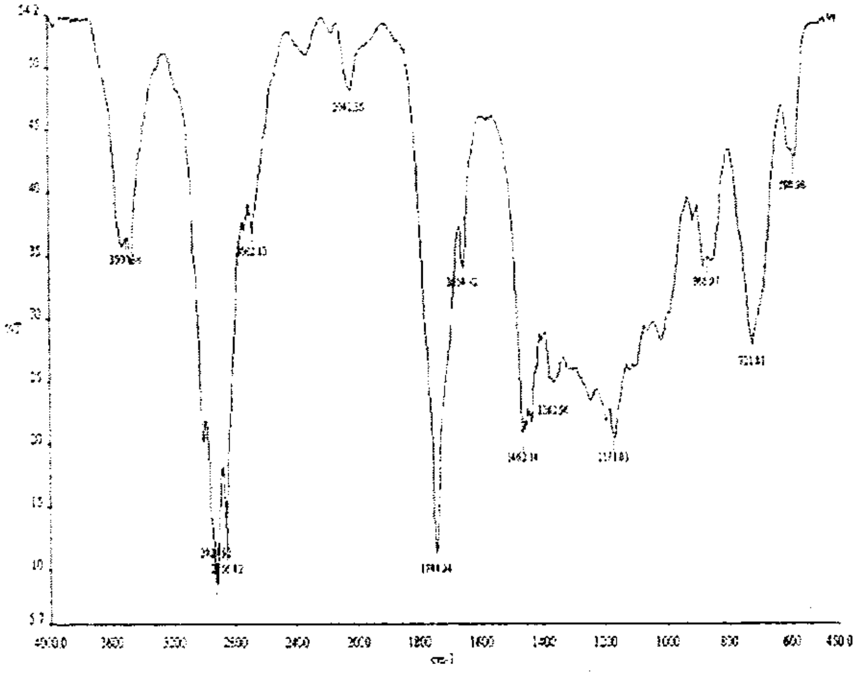
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