OIL EXTRACTION TECHNIQUES FOR BIOENERGY PRODUCTION:

A SYSTEMATIC REVIEW

Maria Ameen[1], Mushtaq Ahmad[1], Muhammad Zafar[1]*, Shazia Sultana[1]

ABSTRACT

Ecological issues and fossil fuel depletion have boosted research in field of sustainable bioenergy development. For biofuel production, oil extraction is key factor related to energy consumption as well as product value. This review focuses on recent advances and prospects in oil extraction techniques used in biofuel production. Major traditional oil extraction practices involve conventional solvent extraction and modern techniques from plants include supercritical fluid extraction, physical supported solvent extraction and novel techniques for oil extraction. This comparative study addresses conventional and modern oil extraction techniques from plants based feedstock for biofuel synthesis. This concise and systematic review covers advancement of extraction methods related to feedstock used in manufacturing various generations of targeted fuel.

Keywords; Biofuels, Bioenergy, extraction techniques

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[1]Biofuel lab, Department of Plant Sciences, Quaid-i-Azam University, 45320 Islamabad, Pakistan.

zafar@qau.edu.pk (*corresponding author)

INTRODUCTION

Primarily, world's energy demands are still served by fossil fuels that account for >88% of chief energy consumption (Agarwal et al., 2018). These current non-renewable energy sources will be no longer available and forewarnings about probable depletion of such cheap petroleum based fuels have been issued (Sipra et al., 2018). Additionally, various greenhouse gases such as CO_2 emissions due to fossil fuel combustion are posing serious environmental issues. Hence, the reduction of greenhouse gas affluences from fossils and production of potentially sustainable and renewable sources has become hot issue and essential topics across the globe (Pradhan et al.,2018). The primary sources of energy that is derived from natural phenomena such as wind, water and solar energy (Manouchehrinejad et al., 2018). Biomass is another primary source of energy after coal and oil therefore various technological possibilities for conversion of biomass into biofuel have been studied and implemented practically. Generally, biomass is converted into fuel via biological, thermochemical and physico-chemical approaches. Biological methodologies such as anaerobic digestion and fermentation yield various products such as bioethanol, biogas and biodiesel. The thermochemical methods include liquefaction and gasification for production of oil and gas, respectively. However, physicochemical such as extraction, esterification and transesterification also involve extraction that permits to recover required constituent or elimination of unwanted components from directed feedstock (Guo et al., 2016).

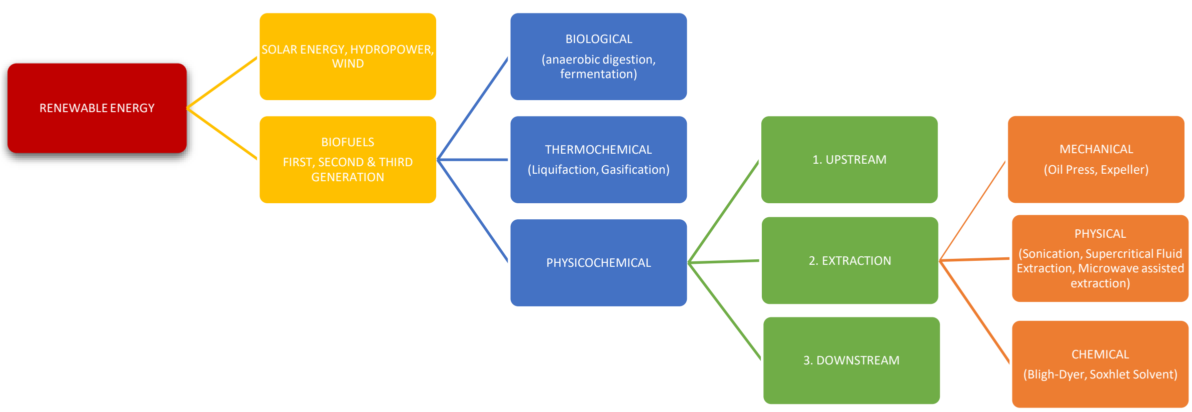

Figure 1. Schematic plan of renewable energy alternatives

Current review is structured around classification of traditional and modern oil extraction techniques and their application on first, second and third generation feedstock for biofuel synthesis.

Basically, in physiochemical process for bioenergy synthesis, extraction usually involves midway phase. **Figure 1**. As upstream procedures should be done before extraction for example cultivation of feedstock and drying process. However, once extraction have been performed then afterwards downstream procedures are performed that involve refining of extracts via fractional distillation, esterification and transesterification. Extraction is done via three basic ways physical, mechanical and chemical approaches (Khan and Hann, 1983). In biofuel production, all three approaches are used but latter two are frequently applied. Various solvents are used for extraction of fueling substances such as hydrocarbons and lipids . Based on specific components and type of biomass, solvent selection from variety of available solvents. Extraction conditions and extraction solvents (selectivity and efficiency) are affected by physical and chemical properties for example polarity (Kanda et al., 2013). Additionally, environmental concerns and economic issues in selection of solvent and application of solvent extraction must be considered. Few demonstrative extractable first, second and third generation feed stocks for production of biofuel are given in table 1. Biofuel products such as biodiesel and jet fuels' precursors are obtained via extraction process. Wood biomass extracts are used to make bioalcohol. However, bio-solid fuel is obtained after water removal and purification of biomass through extraction technologies.

Table 1. Extractable constituents from representative feedstock for synthesis of different generations of biofuel.

Generations of Biofuel	Extraction techniques	Extractable Constituents	Products/ Targeted type of biofuel	References
First generation (Food crops, animal fats)	Conventional solvent extraction.	Fats and Oil	Biodiesel	(Adeoti and Hawboldt , 2014)
Second generation	Mechanical, Conventional solvent extraction, Supercritical fluid	Hydrocarbons Fatty acids Biosolids	Jet fuel Biodiesel Solid fuel	(Mortimer et al., 2012) (Roschat,2017)

(Non-food crops)	extraction, Physical supported solvent extraction.			(Li et al., 2014)
Third generation (Algae)	Supercritical fluid extraction, Physical supported solvent extraction.	Hydrocarbons Fats	Jet fuel Biodiesel	(Lovejoy,2013) (Lohman,2013)

Classification of extraction techniques

Generally, extraction techniques are classified as mechanical, chemical and physical methods used for synthesis of biofuel. Mechanical extraction is done without using any chemical along with different advantages for example low equipment price and directly useable crude oil. Particularly, the use of expellers or presses are used for mechanical oil extraction from oleaginous material. Contrariwise, such methods are used rarely for synthesis of other two generations of biofuel. In extraction process, physical techniques involve microwaving, heating homogenizing and sonication whereas chemical method primarily involves use of various solvent for extraction from targeted feedstock that comprises of use of soxhlet extractor, classical liquid-liquid extraction and conventional bligh-dyer method. Unlike mechanical methods, application of chemical and physical methods is done at a time and physical methods are generally applied for solvent extraction. Hence, in this review for comprehensive assessment of chemical and physical methods have been categorized as conventional solvent extraction (CSE), supercritical fluid extraction (SFE), Physical supported solvent extraction (PSSE). Additionally, new methods of oil extraction have been classified as novel techniques (Li et al., 2019).

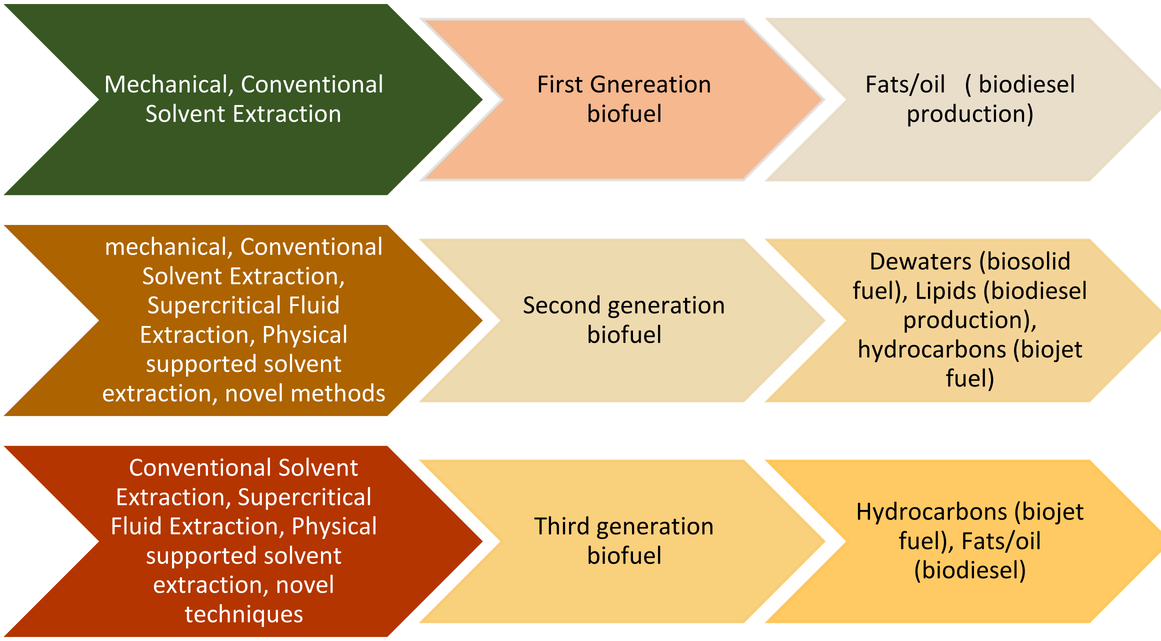

Figure 2.**Extraction methods for different generations of biofuels along with targeted constituents.**

Conventional Solvent Extraction

Traditional technique i.e. CSE has been often used extraction method for times and various reports have mentioned it. A prominent technique known as chemical solvent extraction is practiced conventionally in several fields such as pharmaceutical industry and food and such techniques have been verified. For conventional solvent extraction methods, solvents with high solubility and high selectivity are used at room temperature and ambient temperature in order to obtain desired composition. Some classical and conventional extraction methods include Bligh Dyer method and soxhlet apparatus that are being used frequently for oil extraction from solid feedstock Soxhlet extractor was invented by Franz Von Soxhlet and it is used for components that are less soluble and impurities are insoluble in solvent (methanol, chloroform and n-hexane) **Figure 3** shows electric oil expeller used conventionally for mechanical oil extraction whereas soxhlet apparatus for chemical oil extraction.

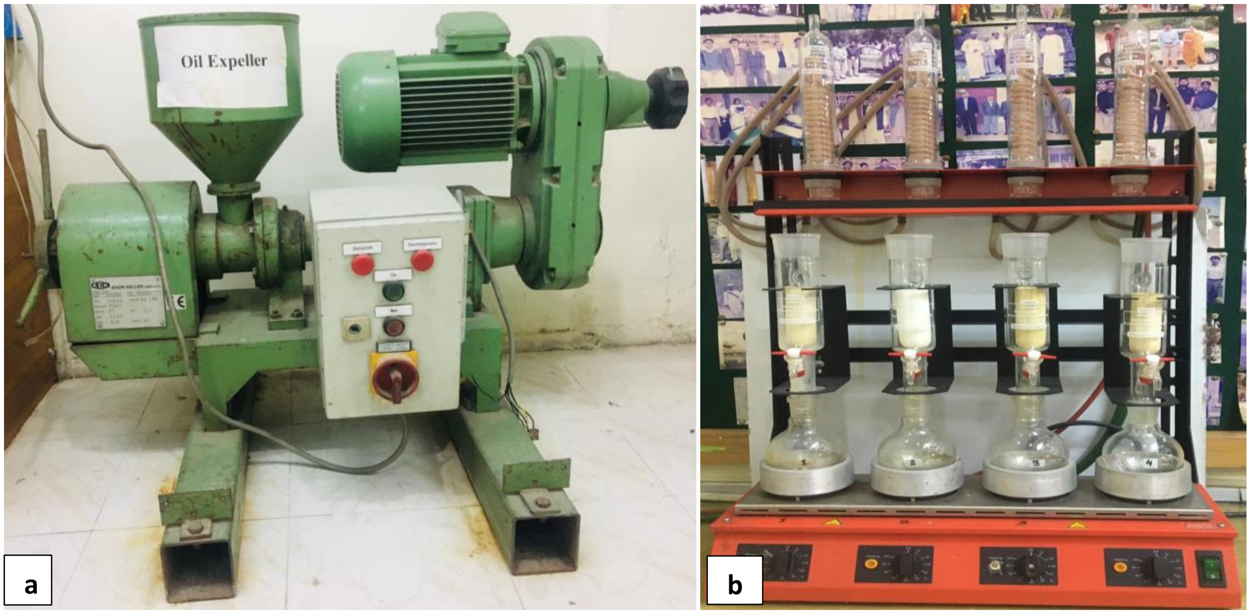

Figure 3(a) Mechanical oil extractor (b) Soxhlet Apparatus

Merits of this procedure include prevention of solvent saturation with extracted material and analytes get eradicated from extracting liquid. Repeated procedure is performed that's why sample with fresh portion remain in contact with solvent and boiling point of solvent is selected as temperature of the system. It is highly adapted even with many shortcomings like sample dilution with huge amount of solvent and requires many hours and days. A blend of solvents is utilized in Bligh-Dyer method and possibility is still there to alter this combination depending on polarity of fats within targeted material (Kou and Mitra (2003). For biofuel production, different organic solvents have been reported. The principle of Conventional Solvent Extraction in field of biofuel production is that organic solvent in contact with biomass, the component to be extracted solubilizes into organic solvent due to solubility of biomass in organic solvent. Hence, an appropriate solvent with high solubility and biocompatibility for targeted constituents is preferred. Nevertheless, demerits of conventional solvent extraction include use of organic solvents that are environmentally hazardous and dangerous for health. Furthermore, pretreatment is necessary in Conventional Solvent Extraction (CSE) for the extraction of available constituents and this pretreatment increases the total cost of process

Modern techniques

Physical supported solvent extraction

Sonication and microwave methods are most frequently used in physical methods along with conventional methods. Microwaves, electromagnetic radiations with 0.3-300GHz frequency, are applied in order to disrupt plant cells at small scale However, sonication has been studied for many years with to disrupt plant cells along with oil extraction. The cavitation of ultrasonic waves is more robust as well as intense at 18-50 kHz frequency (much lower) and medium conditions, for instance, temperature along with viscosity affect the sonication efficiency (Vinatoru, 2001). Physical supported solvent extraction (PSSE) is meant for integration of pretreatment practice into conventional solvent extraction. Due to pre-treatment before biofuel synthesis, use of physical supported solvent extraction (PSSE) is reliant on type of biomass. For instance, microwaves destroy the biomass owe to generation of high frequency waves via sock induction. Hence, it has been recently designated as efficient method for oil containing plant cell disruptions(Pragya et al., 2013).. Moreover, it has been used for disruption of cell membrane and cell wall of microbial cells through cavitation extensively.

Supercritical Fluid Extraction

SFE is oil extraction methodology that developed in 1980s. Owe to high selectivity this method has unique advantage. Supercritical Fluid Extraction involves utilization of fluid as extracting solvent in supercritical stage. The thermal and physical properties of this fluid are between gas and pure liquid. Water and carbon dioxide are utmost frequently used supercritical fluids. This method has several merits such as extraction of lipids (non-polar constituents) from biomass(Akalm et al., 2017). However, demerits of recently used supercritical fluid extraction methods include safety issues and high operational expenses. For example supercritical CO_2 has operating pressure and temperature above 7.39 MPa and 304.25 K respectively. Therefore, for reduction of expenses, recent studies have been done for use of sub critical or near critical solvents such as water.

Novel Techniques

Few techniques that do not fall in formerly demarcated categories have been stated as novel techniques in this review. Such as:

- Multiple ionic liquids have been evaluated to check their ability in aqueous media for extraction of branched hydrocarbons. (Simoni, 2010).

- Ozonation is another oil extraction method for production of saturated hydrocarbons from algae (Kamaroddin,2016).
- Microalgal oil can be extracted via solvents having switchable hydrophilicity (Boyd, 2012).
- Solvents like Dimethyl ether with liquefied gases have been used for extraction from wet biomass and dewatering of biofuel simultaneously(Li et al.,2014).

Extraction techniques based on feedstock

Extractable components of different feedstocks for synthesis of various generations of biofuel are mentioned in **Table 1**

Extraction techniques for feedstock of first generation biofuel

Animal fats and arable food crops are feedstock for production of first generation biofuel as such crops and animals are source of sugar, starch, fats and oil that derives bioenergy synthesis reactions. Sugar cane, corn, wheat and oily crops are most common sources for two chief classes of first generation biofuel i.e. biodiesel and bioethanol. Particularly biodiesel, defined as fatty acid methyl esters, is synthesized via transesterification of triglycerides derived from oils of feedstock plants. Conventional solvent extraction and mechanical methods are collectively applied for extracting oil effortlessly from food crops for first generation biofuel. The application of specific method for oil extraction for synthesis of first generation biofuel depends on mechanical techniques as extraction of oil from plant seeds (account for large portion of first generation biofuel) is usually done via mechanical pressers as shown in **Figure 2**. (Oyinloda et al., 2004). Therefore, first generation biofuels are considered to exhibit environment as well as economical limitations and consequently fewer researches have been carried out in development of mechanical oil extraction First generation biofuel is no more an innovative research subject matter due to its competition with world's food supply creating food security issues (Garcia, 2017; Koizumi, 2015).

Extraction techniques for feedstock of second generation biofuel

Fuel, which is manufactured from different kinds of biomass that is not only obtained from edible but also non-edible feedstock. Industrial, agricultural, civil residues and wastes as well as lignocellulosic biomass offer comparatively more difficulty in extraction of desired fueling substances. Particularly, production of desired fuel is especially challenging via merely extraction techniques from wood lignocellulosic biomass. Consequently, techniques to extract bio-oil stated in research articles recently are alternate to those performed for residues from industries, civil agricultural lands. As second generation feedstock, the utilization of extractable woody plants oil has been reported for biodiesel fuel contrary to first generation feedstock (predominantly arable crops) (Branco et al., 2019) . Figure 2 shows procedures for extracting oil from sources of second generation biofuel that miscellaneous products are manufactured. Certain mechanical techniques have been performed for second generation feedstock as oil content is not as much of first and third generation biomass due to poor oil's recovery rate in case if just mechanical method used. Fish oil based biofuel has been derived from waste of fish processing plant and subsequently oil was recovered via soxhlet extraction (Conventional Solvent Extraction) and carbon dioxide (supercritical fluid extraction) (Jayasinghe and Hawboldt, 2013). Various chemicals specifically organic solvents have been recognized as agents of oil extraction for synthesizing the 2nd generation biofuel, as shown in Table 2.

Table 2 Representative organic solvents for second generation biofuels

Organic Solvent	**Feedstock**	**Constituents extracted**	**Yield**	**References**
n-hexane	Rubber seed	Bio crude Oil	20.4 wt.%	(Roschat, 2017).
dichloromethane			16 wt.%	
Acetone			18 wt.%	
Hexane	Tobacco	Hydrocarbons	6.28 μg mg^{-1} FW	(Mortimer et al., 2012)
Petroleum ether			5.69 μg mg^{-1} FW	
Chloroform			6.20 μg mg^{-1} FW	

Wt. weight.FW, fresh weight.

Case studies between extractable components and polarity mediated by three commonly used aprotic or non-polar solvents; petroleum ether, chloroform, n-hexane have been used as solvents in order to extract various hydrocarbons and overall 5.6, 6.2 and 6.2 $\mu g mg^{-1}$FW (fresh weight) hydrocarbon yield was obtained, respectively, from *Nicotiana glauca* (Mortimer et al.,2012)

Whereas, extraction of oil of *Hevea brasiliensis* (Rubber seed) was done by mixing with solvents (polar or non-polar); dichloromethane, acetone or hexane for optimum time of 30 minutes at 25℃ and extraction yield of total crude oil 16%, 18 wt.%, 20.4%, respectively (Roschat, 2017). .Usually, extraction solvent is selected by following premise "Like dissolves like". Difference in polarity of solvent used determines composition of biofuel from same feedstock. As a Physical supported solvent extraction method, ultrasonic associated extraction has been done for biofuel (liquid) synthesis from seeds of *Jatropha curcus.* This technique is effective in potential reduction of recalcitrance of cellulose, hemicellulose and lignin i.e. lignocellulosic mass and enhances their aptness as bioethanol feedstock (Shuhairi et al., 2015). Contrastingly, supercritical fluid extraction (SFE) method when applied to lignocellulosic biomass, reflected as appropriate for it; due to high resolvability of this technique and researches related to SFE for biofuel from lignocellulosic biomass were done via methanol or ethanol. Remarkably, second generation biofuel are affected considerably by extraction parameters during the use of supercritical fluid extraction, for instance, time, temperature, solvent/biomass ratio and operating pressure during extraction procedure. Furthermore, a highly cost effective and eco-friendly novel technique by use of gas (liquefied) performed in normal reaction conditions i.e. temperature and pressure, stated in various research reports related to crude fuel of biological origin, gained from industrial waste as well as crop biomass (Sakuragi, 2016).

Extraction techniques for feedstock of third generation biofuel

Microalgae are considered as main source for third generation biofuel hence termed as algae biofuel that has been appeared not only as potentially renewable alternative source for biofuel synthesis but also highly feasible feedstock that overcomes the shortcomings of feedstocks of other two generations of biofuels. Several diverse types of renewable biofuels include hydrocarbons, biohydrogen and biodiesel are being synthesized from algae. There are several merits for manufacturing fuel based on algal origin because biodiesel yield is fifteen to three hundred times more than conventional crops on area basis (Schenk, 2008). Additionally, algal harvesting cycle is short with high growth rate and no high featured agricultural lands are needed for production of algal biomass (Dragone (2010). Due to these assured merits, algal biofuels have received great attention globally. In contrast to terrestrial oily plants, oil expellers and presses cannot aid in mechanical extraction of algal oil due to intricate cell membrane, small cell size and rigid/thick cell wall (Ru an, 2006) . Therefore, different alternate oil extraction methods are under consideration to get fueling substances effectively from pro-treated or fresh algae because algal biofuel is still in progress. Biofuels synthesized from algae via extraction procedure principally comprise bio-jet fuel and biodiesel, with such production depends on diverse components biosynthesized by different microalgal species. Figure 2 shows various extraction techniques for third generation feedstock; these are conventional solvent extraction, supercritical fluid extraction, Sonication, microwaving and liquefied gas that extract components like hydrocarbons for biojet fuel and lipids (saturated and unsaturated) for biodiesel synthesis (Balasubaramanian et al., 2013; Byreddy et al., 2015).

Table 3. Oil extraction techniques for biofuel production from algae (Third generation biofuel).

Technique	Solvent Used	Optimum Condition	Algae	Constituent extracted	Yield (%)
Soxhlet	Methanol: Hexane (2:3)	Normal Pressure, Temp (70℃)	*Nannochloropsis oculata*	Lipids	30
Bligh-dyer	Methanol: Chloroform	Normal Pressure, Temp (25℃)	*Schizochytrium sp.*	Lipids	22.1

Supercritical fluid extraction	$SCCO_2$	Pressure (15MPa), Temp (40℃)	*Tetraselmis sp.*	Lipids	10.8
Sonication	-	(50kHz), Time (15 minutes)	*Chlorella sp.*	Lipid	25.5
Microwave	-	Pressure (15MPa), Temp (100℃)	*Botryococcus sp.*	Lipids	28.5
Liquefied gas	Dimethyl ether	Pressure (0.51MP)	*M. aeruginosa*	Bio-oil	40.1
		Temperature 25 ℃,	*B. raumii*	Hydrocarbons	40.9

Conclusion

This review discusses currently published articles in biofuel production concerning research on extraction process and is envisioned to overcome deficiency produced due to want of relevant published articles. For clarification of emerging and multiple existing techniques primarily utilized chemical and physical methods categorized as CSE,SFE,PSSE and novel techniques. Ideally, SFE retain merits as compared to PSSE and traditional CSE such as organic solvent is excluded therefore along with high extraction speed, the risk of storage is also reduced. Nevertheless, supercritical fluid extraction technique is still used in pharmaceutical and food industries. At this stage this method has technical bottleneck in field of biofuel production owing to insufficient cost.

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