Review on the Extraction Methods of Crude oil from all Generation Biofuels in last few Decades

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Abstract:
The ever growing demand for the energy fuels, economy of oil, depletion of energy resources and environmental protection are the inevitable challenges required to be solved meticulously in future decades in order to sustain the life of humans and other creatures. Switching to alternate fuels that are renewable, biodegradable, economically and environmentally friendly can quench the minimum thirst of fuel demands, in addition to mitigation of climate changes. At this moment, production of biofuels has got prominence. The term biofuels broadly refer to the fuels derived from living matter either animals or plants. Among the competent biofuels, biodiesel is one of the promising alternates for diesel engines. Biodiesel is renewable, environmentally friendly, safe to use with wide applications and biodegradable. Due to which, it has become a major focus of intensive global research and development of alternate energy. The present review has been focused specifically on biodiesel. Concerning to the biodiesel production, the major steps includes lipid extraction followed by esterification/transesterification. For the extraction of lipids, several extraction techniques have been put forward irrespective of the generations and feed stocks used. This review provides theoretical background on the two major extraction methods, mechanical and chemical extraction methods. The practical issues of each extraction method such as efficiency of extraction, extraction time, oil sources and its pros and cons are discussed. It is conceived that congregating information on oil extraction methods may helpful in further research advancements to ease biofuel production.

1. Introduction:
The ever growing demand for the energy fuels, economy of oil, depletion of energy resources and environmental protection are the inevitable challenges required to be solved meticulously in future decades in order to sustain the life of humans and other creatures in this world. Switching to alternate fuels that are renewable, biodegradable, economically and environmentally friendly can quench the minimum thirst of fuels demands, in addition to mitigation of climate changes. At this moment, production of biofuels has got prominence [1]. The term biofuels refer to the fuels derived from living matter either from animals or plants, specifically concern to Biodiesel and Bioethanol. Biodiesel is nothing but mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Triacylglycerols or colloquially triglycerides are the precursors from which biodiesel has been produced. Triacylglycerols are one of the forms of lipids. For the extraction of lipids (oils or fats), a major component for biodiesel production, several extraction techniques have been put forward. Triglycerides
are converted into biodiesel by tranesterification using alcohol with or without a catalyst. Biodiesel is being used as one of the promising alternate fuel sources for diesel engines [2-4]. Biodiesel is renewable, environmentally friendly, safe to use, biodegradable and it has become a major focus on intensive global research and development of alternate energy. Although the composition of biofuel is complex, it includes mainly palmitic acid, stearic acid, oleic acid, linoleic acid and other fatty acid esters [5-7].

2. Generations of Biofuels:
Hitherto, an immense research in the exploration and development of alternate biofuel resources with desired qualities has been carried out. Based on the resource type, four generations of energy crops have been categorized as first, second, third and fourth generations.

**The First Generation biofuels** are produced directly from food crops by extracting oils as raw material for biodiesel or bioethanol production through transesterification and fermentation respectively. Bioethanol, fatty acid methyl ester (biodiesel) and pure plant oil are the different types of biofuels currently play a major role at the global level, all belong to the first generation fuels [8]. Crops such as wheat and sugar are the most widely used feed stocks for bioethanol, while rape seed has been proved a very effective crop for biodiesel. However, first generation biofuels have a number of associated problems. There is a serious debate over their actual efficacy in reducing greenhouse gases (GHG) and CO₂ emissions due to the fact that some biofuels can produce negative net energy gains, releasing more carbon in their production than their feedstock’s CO₂ capturing capacity during their growth. However, the most contentious issue with first generation biofuels is ‘fuel vs food’. As the majority of biofuels are produced directly from food crops, the rise in demand for biofuels has led to an increase in the volumes of crops being diverted away from the global food market. This has been blamed for the global increase in food prices over the last few years. This is the foremost reason for the inception of second generation fuels [9-11].

**Second Generation** biofuels have been developed to overcome the limitations of first generation biofuels. They are produced from non-food crops such as wood, organic waste, agriculture waste and specific biomass crops, therefore eliminating the main problem with first generation biofuels. Second generation biofuels are also aimed at being more cost competitive in relation to existing fossil fuel. Life cycle assessment of second-generation biofuels has also indicated that they have increased ‘net energy gains’ compared to first generation biofuels [10, 12-14]

**Third Generation** of biofuels is based on improvements in the production of biomass. It takes advantage of special energy crops such as algae as its energy source. The algae are cultured to act as a low-cost, high-energy and entirely renewable feedstock. It is predicted that algae will have the potential to produce more energy per acre than conventional crops. Algae can also be grown using land and water unsuitable for food production, therefore reducing the strain on already depleting water sources. A further benefit of algae based biofuels is that the fuel can be manufactured into a wide range of fuels such as diesel, petrol and jet fuel. However, scale up of algal systems for biofuel production is not very economical [15, 16].

**Fourth Generation** Bio-fuels are aimed at not only producing sustainable energy but also a way of capturing and storing CO₂. Biomass materials, which have absorbed CO₂ while growing, are converted into fuel using the same processes of second generation biofuels. This process differs from second and third generation production in a way that, at all stages of production, the carbon dioxide is captured using processes such as oxy-fuel combustion. The carbon dioxide can then be geo-sequestered by storing it in old oil and gas fields or saline aquifers. This carbon capture makes fourth generation biofuel production carbon negative rather than simply carbon neutral, as it ‘locks’ away more carbon than it produces. This system not only captures and stores carbon dioxide from the atmosphere but also reduces CO₂ emissions by replacing fossil fuels [17, 18].
This review provides theoretical background on the mechanical and chemical methods of extraction from all generation biofuel sources. The practical issues of each extraction method such as efficiency of extraction, extraction time and type of oil source and its pros and cons are discussed. Finally, potential applications of those extraction methods are reviewed.

3. Methods of oil extraction:

There are three main methods that have been identified for the extraction of the oil/fats/lipids: (i) Mechanical Extraction, (ii) Chemical Extraction (Solvent Extraction) and (iii) Biological Extraction. Most commonly used commercialized methods of oil extraction are solvent extraction and mechanical extraction. Sufficient drying of sources before oil extraction eases the process and improves the extraction efficiency. Oil extraction sources are to be processed depending on the method of extraction. For instance, whole seeds or kernels can be extracted using mechanical expellers or presses whereas, solvent extraction is possible with kernels. On the other side, biological extraction is possible only with the finely crushed sources [2].

3.1. Mechanical Extraction

The most traditional method of oil extraction is the use of mechanical presses/expellers. Mechanical expression is the forceful extraction of oil from the oleaginous material under applied pressure (hydraulic or screw presses).

3.1.1. Ram press. Ram press is most commonly used for the extraction of oil seeds. The primary ram press was designed by Karl Bilenberg in 1985. The design of a ram press mainly consists of a hopper, long pivoted lever and a cylindrical press cage as shown in Figure 1 [19].

![Figure 1. Design of a ram press][19].

The lever moves the piston to and forth inside the cylindrical cage. The movement of piston opens up the entry port of hopper in to press cage, through which seeds can enter in to the cage. Movement of piston backwards closes the entry port and creates a pressure on the seeds so that the oil is expelled from the seeds. Oil drains from the perforations of cage in to the metal bars situated below the cage and compressed seed is pushed out through the gap situated at the end of the cage. Pressure of the system can
be adjusted by managing the gap using adjustable restriction cone. A pressure as equal to small scale expellers can be achieved in ram press. It has the processing capability of approximately 4kg/hour. The ram press is specifically designed for deoiling of sunflower seeds. Currently, ram press is being used for the extraction of oil from groundnuts, copra and sesame. The extraction efficiency of ram presses varies from 57-62% [20]. In case of Jatropha, 65% of oil can be extracted through ram press. Though ram press is found inefficient for large scale oil extraction, still it is being used to produce oil energy source in rural areas [21]. The advantages with the use of ram press are, i) requires minimal operational skill, ii) low maintenance and repair, iii) low cost equipment and iv) simple and affordable in rural areas [22].

3.1.2. Bridge press. The design of a bridge press consists of a press plate, which is placed at the bottom of a screw rod. The setup looks like a nut set that moves in to the bridge of the cage. A single horizontally positioned head bar with two levers moves the screwed rod. Thrust bearing ease the movement of screwed rod against pressure plate. Figure 2 shows the bridge press designed by NRI (Natural Resources Institute) [19].

![Figure 2. Design of a typical bridge press [19].](image)

Pressure development in the bridge press depends on the diameter of cage. Initially, it was designed with 24cm diameter cage that suits to expel oil from palm fruits under low pressures. Due to the flexibility with pressures, bridge press has found application in oil extraction from wide range of seeds. Higher pressures can be obtained by reducing the diameter of the cage as well the pressure plate. Reduction in the diameter of cage leads to reduced loading capacity per batch. Generally, the cage can accommodate 5-30kg of oleaginous material with an average capacity of 20kg. During operation, the cage is loaded with a batch of oleaginous material. With the movement of plunger, pressure creates on the material and oil is expelled out of the perforations of the cage. To maintain the constant pressure throughout the materials, layer plates can be used inside the cage. Pressure is to be increased slowly until the initial dropping of oil from the material. Lab experimentations have revealed that bridge press best suits for the extraction of oil from sesame. In the trials, it was also found that the moisture content influences the oil yield. In the experiments, sesame was ground to paste, pre heated to 50°C and obtained a yield of greater than 70% at 12.7% of moisture content [19].

3.1.3. Hydraulic press. Hydraulic presses are available as electrically powered and hand driven. Figure 3 shows the hand driven hydraulic press [23].
Figure 3. Schematic representation of hand driven hydraulic oil press [23].

The design consists of a hydraulic jack, that connects internally to a piston or press inside a cage. Cage is made of steel plates, where the oil sources are fed. The cage accommodates a perforated pipe to collect and drain the extracted oil into the container. Depending on the load at the hydraulic jack, pressure is created on the material and oil expels out. A typical hand driven hydraulic jack can maintain 10-15 tons of load. Even though suitable only for batch processing, still hydraulic press is being used as most economical and practical way to extract oil from seeds or oleaginous tissues in most parts of the world. Oil extraction in hydraulic press is carried out in such a way that the ground seed powder or wet tissues are arranged in sandwiched layers with the press cloth. Initially, a low pressure is applied and the pressure increases with the decrease in oil content of the material being extracted. A high pressure of 2,000 pounds/inch² can be attained in hydraulic press. It requires an expression time of 1.5 – 2 hr from loading to oil drainage and the input capacity of the press depends on its size as well as mode of operation (either motor or hand driven) [23]. Seed oil extraction in hydraulic press occurs in three stages. In the initial stage, the application of compressive load creates the vacuum by sending out the air. At a critical point, seed experiences the pressure at contact points and results in the expulsion of oil out of the seed. In the second stage, also termed as Dynamic stage, oil consecutively replaces the air and oil flow reaches to the maximum. The final stage starts when the drainer volume is completely occupied with the flow of oil [24].

3.1.4. Ghani. Ghani is a traditional motor and pestle device extensively being used in Indian subcontinent for the extraction of oil from groundnuts, mustard, sesame and copra. Mode of oil extraction in ghani is initial grinding of oil seed to fine powder followed by extraction, which differs from the other mechanical devices. The mortar is usually made of wood and is fixed to the floor. Pestle is made of either wood or stone. Initially, these ghanis were driven by a bullock that makes the rotation of pestle through a lever. Movement of bullock around the mortar causes the grinding of seed by pestle inside the mortar. Grounded seed is added with a certain amount of water, which hastens up the expulsion of oil from seed with the kneading action of pestle. Extracted oil oozes out of the opening exist at the bottom of the mortar. Depending on the amount of oil ejected from the seed cake, cake is removed and fresh batch of seeds will
be loaded to the mortar. Bullock driven ghani has the capacity of 10kg seed/2hr. Motor driven ghannis (power ghannis) are found to be efficient compared to bullock driven ghannis, as the animals become tired of working continuously for 3-4hr. Usual throughput of motor ghannis is about 100kg seed/day. Use of ghannis for oil extraction is advantageous as they do not require costly equipment. In addition, no pretreatment of seeds is required and the extracted oil stands for its quality. Figure 4 shows a typical power ghani set up [19].

![Diagrammatic representation of power ghani](image)

Figure 4. Diagrammatic representation of power ghani [19].

3.1.5. *Continuous Screw Presses or Expellers.* Expellers have found worldwide applications and are commercially being used as most common mechanical oil extraction equipments. They are commonly used for the expulsion of oil from cotton seeds, flax seeds, palm kernals, peanuts and most of the other seeds depending on their availability for continuous operation. Figure 5 shows the design of a screw expeller [25].
Figure 5. Design of screw expeller [25].
The heart of the machine consists of a horizontal shaft, which accommodates a rotating screw. The screw rotates inside a closed cage formed by steel bars. Oil seed is fed continuously into the hopper, which directs the seeds into the cage. A movable cone lies at the discharge end maintaining the pressure by adjusting the width of annular space. Spacers allow the passage of oil with the increase in pressure. Hand wheel placed at the other end of the screw is used to adjust the choke. Choke size and rotation of axis are to be adjusted based on the type of seed used for extraction [24]. Screw press expeller operates on a principle that, revolving worms forces the oil seed through the barrel, thereby, causing the reduction in the volume occupied by seeds. Further reduction causes the compression of the seed cake and expulsion of the oil. Oil drains out through the perforated lining bars and the compressed cake is ejected out via annular orifice [26]. Oil extraction efficiency of expeller is determined by the residual oil content in the cake. This efficiency largely depends on the pressure and speed of the rotating shaft. Operation at high pressure leaves the cake with less than 10% oil but increases the crude nature of the oil, which requires further tedious purification steps. The other side, reduction in the speed of the shaft causes the oil loss in the cake and also increases the solid particulate (cake) content in the oil [27]. An expeller press can exert more pressure than a hydraulic press can. The ability to attain increased pressures will improve the oil extraction efficiency of an expeller. The seed cake from a hydraulic press contain 4-6% residual oil whereas, seed cake of an expeller contains only 3-4% of left out oil. Though conventional, expellers are hitherto playing a vital role in the oil expression plants. The disadvantage associated with expellers is, longer duration of operation is needed to achieve higher efficiencies. Expellers are also used in combination with solvent extraction (discussed further) [23].

Mechanical methods are the most conventional methods for oil extraction. Avoiding the use of chemicals, high quality and instantly consumable crude oil production are the main advantages associated with mechanical modes of extraction. In addition, mechanical extraction involves low equipment cost, low power requirement and also manual skills compare to other methods. However, on considering the efficiencies, mechanical method is facing the limitations of low yields and high oil content in the residual cakes. These drawbacks make the extraction an unprofitable one with mechanical systems [24].

3.2 Chemical Extraction
Chemical extraction methods mostly involve organic solvents. Hence, chemical extraction is also termed as solvent extraction. Solvent extraction is mostly widely used and commercial method for the separation of oil and fats (lipids). Though the effect of ultrasound waves and microwaves is mechanical, the current review considered ultrasonic assisted extraction and microwave assisted extractions under solvent extraction as mostly these techniques are being used in conjunction with the use of solvents.

If it is intended to extract high yield of oil from the oleaginous material using mechanical methods, the oil source has to be dried to low moisture content or exposed to high temperatures, resulting in the darkening of extracted oil. On the other hand, during extraction by most of the expellers or presses, the meal which can be used as fodder or human nutritional food will experience high temperatures and make it unsuitable for the purpose. In addition, mechanical method of extraction has low efficiency and leaves high oil content in the seed cake. Mechanical methods are found unsuitable for complete oil extraction from low oil containing seeds such as soybeans. To overcome the disadvantages associated with mechanical methods, solvent methods have been developed. Even, solvent extraction is extensively being used to extract residual oil present in the seed cake from mechanical extraction [28]. Solvent extraction is the isolation of specific or desired components from solid or liquids by using a solvent. There are different types of solvent extractions, most common are liquid – liquid and solid-liquid extractions. The focus of this review is circumscribed to solid-liquid extraction as most of the oleaginous materials are solids and are directly used for oil extraction.

Chemical properties of the extractant as well as the analyte influence the phenomena of extraction. Mostly, solubility, hydrophobicity or hydrophilicity, vapor pressure, molecular weight and acid dissociation are the fundamental properties of an analyte that decide the selection of solvent for extraction [29]. Particle size (reduced particle size limits the barrier between two phases), agitation speed and temperature of extraction influences the efficiency of the solvent extraction.

3.2.1. Folch method. Individual organic solvents or combinations of organic solvents are used to extract specific class of lipids from a mixture of organic compounds. Folch and firm had developed a solvent lipid extraction method from animal tissue with the use of Chloroform and methanol (2:1 volume basis). The procedure of Folch et al [30] method is as follows; initially the cells (mostly tissues) are homogenized and equilibrated with 25% volume of saline solution, followed by rigorous mixing. The resultant mixture on gravity separation forms two distinguished layers, where the upper phase accommodates lipids. Folch et al method is the oldest method for lipid extraction and forms the basis for the development of existing advanced solvent extraction methods. Though the method is rapid and ease, less sensitive compared to other total lipid extraction methods.

Bligh and Dyer method:

It is the widely adopted method for the extraction of lipids and the mode of extraction is similar to that of Folch et al method. The main difference between the Folch and Dyer methods is the difference in the solvent/solvent and solvent/tissue ratios. Bligh and Dyer [31] method involves the simultaneous extraction and separation of lipids. In addition, proteins form a precipitated layer between the two liquid phases. The procedure involves the use of chloroform and methanol in 1:2 (v/v) and finally the lipids can be further separated from the chloroform phase. This method is most widely being used for the extraction of lipids or fats from third generation biofuel sources (algae). To improve the efficiency of this method, researches have adopted the use of one molar NaCl as an alternate to water. The use of NaCl prevents the
binding of acidic lipids to the denatured lipids. Later, it was found that the addition of 0.2M phosphoric acid and HCl reduced the separation time of lipids [32].

3.2.2. Soxhlet extraction. Soxhlet extraction is one of the most traditional techniques still being used for the separation of a wide range of volatile compounds to oils from solid samples. In mid 19th century, Baron Von Soxhlet has introduced this method, after whom the method is named. Soxhlet extraction is a popular method and is being considered as a reference for several existing modern extraction techniques.

Figure 6 [33] shows the set up of a typical Soxhlet apparatus, mainly consists of a round bottom flask, a thimble holder and a condenser.

![Figure 6. Soxhlet extraction apparatus set up [33].](image)

The mouth of round bottom flask is fitted with the Soxhlet thimble, which is connected in the other side with a condenser as shown in figure 6. Operation is very simple and at first, the Soxhlet thimble is loaded with a cellulosic pack of oleaginous material. Extraction solvents are used as individual or mixture of solvents; hexane, ethanol [34], chloroform and methanol, hexane and methanol [35], terpene [36], 2-propanol, chloroform, toluene [37]. Most commonly hexane is used for oil extraction, added to the flask and the flask is heated slowly to the boiling point of the solvent so that the solvent vaporizes. Soxhlet extraction is based on the principle that, the vaporized solvent passes through the side arm, condenses at the condenser and floods in to the thimble. When the moderately hot solvent interacts with the oil source in the thimble, extraction of analyte (oil, lipid, fat or phytochemicals) occurs and the solvent with analyte drains again in to the flask through the siphon device. Repetitions of the cycle will result in complete extraction of the analyte. Analyte gets accumulated at the bottom of the flask, as it has higher boiling point than the extraction solvent. Consequently, at each cycle material being extracted will interact with fresh solvent. Soxhlet extraction is a slow process and requires further separation of solvent to get analyte, an energy intensive process. The considerable disadvantages associated with Soxhlet extraction are, selection of solvent, longer duration of extraction and large quantity of solvent consumption. Even though being a reference method, in recent days, with the prevalence of modern extraction techniques, Soxhlet extraction is becoming an outdated extraction technique [33, 38].
Different solvents yield different natural compounds from the material taken and also the extract composition differs from solvent to solvent. Therefore, selection of a solvent for oil extraction is a most critical step for Soxhlet extraction [39]. Hexane, an extensively used solvent for oil extraction has peculiar characters such as excellent oil miscibility, distinguishable boiling point range (63-69°C) and easily recoverable. However, the Environmental Protection Agency (EPA), USA has categorized n-hexane as top most hazardous solvent among 189 air pollution causing solvents [40]. This is also one of the challenges experienced by Soxhlet extraction.

3.2.3. Supercritical fluid extraction (SFE). In general, solvent extractions (Soxhlet) are associated with the limitations of longer durations, large quantity of solvent requirement and incomplete expulsion of hexane from the oil. Hence, finding alternate innovative technologies that could overcome these limitations is imperative [41]. In considering the environmental issues tagged with solvent extraction, U.S E.P.A has promoted the pollution prevention technologies through green chemistry. Initially, in 1980’s, SFE has been developed as laboratory method and an alternate to organic solvents use for the extraction of lipids. Later, it has been developed as an industrial scale technique and subsequently replaced the usual direct solvent extraction methods. Gases such as CO₂, propane, toluene, ethane and water are used as solvents in SFE at their supercritical conditions. A gas at supercritical conditions possesses the properties such as density and solubility as a liquid whereas, viscosity, diffusivity and surface tensions similar to that of a gas. These changes in the properties improve the selectivity, flow rates and mass transfer than the normal solvents. In addition, the use of these gases as solvents in SFE makes the extraction more efficient and environmentally benign when compared to conventional solvent extractions [42].

Carbon dioxide (CO₂) is the most commonly used oil/lipid extraction solvent in SFE owing to its acceptable critical conditions (temperature 304°K and pressure 73atm), low cost, non flammability and non toxicity [43]. The properties of supercritical CO₂ for the extraction of oils and fats are summarized as, 1) high solubility of non polar compounds, 2) high dissolution of low molecular weight components, 3) high affinity towards oxygen containing organic substances, 4) less solubility of water at <100°C, 5) Less affinity towards proteins, polysaccharides and other salts and 6) Compound of interest can be extracted by adjusting temperature and pressure [44]. Figure 7 shows the schematic representation of Supercritical CO₂ apparatus [24].

![Schematic representation of Supercritical CO₂ fluid extraction](image-url)
pumps. The temperature of extraction chamber is maintained through heating jacket and thermostat. Back pressure valve is helpful to regulate the pressure. The supercritical CO$_2$ interacts with the material in the extraction chamber and the extracts are collected in collector. Reduction in pressure lightens the CO$_2$, leaving the extracts in the collector and the CO$_2$ is circulated for further extraction [45].

The principle involved in the SFE is that, when a solvent at its supercritical conditions interacts with oleaginous sample, dissolution of oil occurs in to the solvent. The soluble oil can be separated from the supercritical fluid by reducing the pressure. Factors such as temperature, pressure and extraction time influences the extraction efficiency and also purity of the oil. When considering the total lipids, almost all the lipids dissolve in the supercritical fluid, makes the separation process difficult. Usually adsorbents such as silica, celite and synthetic resins are used to enhance the separation of soluble lipids from supercritical CO$_2$ [44]. Even though supercritical CO$_2$ extraction is efficient than other solvent extractions and yields quality oil, still the technique is in its infancy and has not found wide commercialized applications for the extraction of oils. High equipment and operation costs are predominant reasons for non commercialization of the technique. Research is being carried out to optimize the process parameters, there by the reduction of process cost [24].

3.2.4. Ultrasound assisted extraction (UAE). As conventional solvent extraction methods have limitations of longer duration of extraction, toxic solvents usage and low efficiency, investigations have reported that combination of mechanical waves with the solvent extraction techniques can transcend these barricades. Lately, ultrasonics have received a greater attention to use in the extraction processes from medicinal tinctures to industrial biodiesel production [46]. Ultrasonic extraction can be brought about in lab scale by using ultrasonic cleaning bath (indirect) and ultrasonic probe or horn (direct) systems. Ultrasonic reactors are used for industrial applications. Figure 8 represents the bath (a) and probe (b) ultrasonication systems [47].

![Figure 8. Diagrammatic representation of Ultrasonic systems a) bath cleaning and b) probe [47].](image)

The set up of both the systems should be provided with a mechanical agitator and cooling bath to control the rise in temperature during extraction. The bath system contains transducers attached at the base to provide ultrasound waves. The probe system has ultrasonic transducer fitted in to the extraction chamber. During the direct extraction, the probe must be in contact with the solvent medium but not the material being extracted because, the solid material may clog the probe [47].
The extraction is facilitated by two physical phenomena; diffusion through the cell walls and washing out of intracellular contents through the broken walls. The walls of glands or cells are said to be very sensitive (mostly plant based) and are easily breakable upon exposure to ultrasound. This forms the basis for the extraction of fats and lipids as well as essential oils from variety of materials. The efficiency of the process can be increased by reducing the size of the material, which improves the solvent interaction with the material and there by the cavitation assisted extraction. Ultrasonic system either bath or probe when used for the extraction of dried samples, the extraction is not only brought about by mechanical means. It involves two stages, at first, the material is steeped to facilitate swelling and hydration processes. In the next stage, the intracellular contents are transferred in to the solvent by diffusion and osmosis phenomena. Extraction efficiency of ultrasonic assisted process is found higher than the extraction facilitated through mechanical stirring [46,47].

The principle involved in ultrasonication is based on the phenomenon of cavitation. When high frequency (20kHz) ultrasound waves are pulsed in to the sample containing solvent medium, bubbling occurs throughout the medium. The grown bubbles with negative pressure implode at the surface of the cells, causing a mechanical stress on the cells. Collapse of cavitation bubble at the surface of cells causes cell wall damage and leads to the transfer of intracellular contents to the solvent medium. During the process of bubble implosion, shock wave impulses are generated and which creates a microenvironment of high temperature and pressure at the surface of the sample. These shock waves and energetic micro liquid jets enhance the solubilization of metabolites in to the solvent medium and hence improve the extraction [48, 49]. The efficiency of ultrasonic extraction depends on the temperature, frequency of waves and duration of ultrasonication [49]. UAE can be applied to both solid and liquid samples but care should be taken while using solid samples. Cavitation bubble collapse may cause decomposition of analyte if entrapped in to the bubble. Even though ultrasonic assisted extraction is rapid and efficient than conventional Soxhlet extraction, it also involves large quantities of hazardous and expensive organic solvents [50].

3.2.5. Microwave assisted extraction (MAE). In conventional methods of solvent extraction mass transfer of analytes from the sample to solvent is by diffusion and osmotic processes, which limits the rate of extraction. In such conditions, process intensification can improve the extraction kinetics and efficiency. Microwave assisted extraction, an unconventional intensification technique has been developed to improve the yield, quality and efficiency of the conventional solvent based processes. In recent times, MAE has become a promising, economically tenable, simple and efficient process to separate selective compounds at higher rates in less time. MAE is a green extraction technique, which involves the use of water or alcohols as solvents at controlled pressure and high temperatures. Water has high dielectric constant due to its highly polar nature. Hence, traditionally it is not considered as an extraction solvent for non polar organic components. However, at elevated temperatures and controlled pressures, water will attain the properties of alcohols and can dissolve wide range of low to medium polarity compounds during extraction [51]. Figure 9 shows the diagrammatic representation of microwave assisted solvent extraction apparatus [52].
Figure 9. Representation of microwave assisted solvent extraction [52].

The efficiency of a solvent to be used as an extraction medium in MAE depends on the dissipation factor, a measure of solvent ability to absorb microwave energy and dissipate it to the surrounding molecules as heat. Microwave based extraction work on targeting the moisture entrapped in the sample of extraction. When microwave heats up the moisture trapped inside the cells of the sample material, moisture tends to evaporate, thereby creating an extensive pressure on the cell walls through swelling. The inside pressure pushes the cell wall, leads to stretching and rupturing of walls and releases intracellular contents to the solvent. Thus, improves the extraction yield. The efficiency of MAE can further enhanced by using solvents with high heat dissipation capacity [53]. The mechanism of MAE involves the following steps, i) Desorption of analytes from sample matrix under applied pressure and elevated temperatures, ii) Diffusion of extraction solvent in to the sample matrix and iii) Dissolution of analytes in to the extraction solvent. The bolstered efficiency of solvent extraction with the use of microwaves is due to improved solubility of analytes into the solvent, reduction of mass transfer limitations and enhanced disruption of surface equilibrium [38]. Efficiency of MAE depends on solvent nature and volume, extraction time, microwave power, sample particle size, moisture content, temperature and pressure of extraction. MAE has advantages of environmentally friendly, cost effective, low quantities of solvents usage and reduced extraction times. On the other hand, it has the limitations of low efficiency when the extraction solvent or analyte are non polar or volatile. Also, as the technique involves high temperatures, decomposition of thermo labile compounds may occur [54].

4. A few reports on oil extraction for biodiesel production:

Ibrahim et al [55] have designed a screw press and processed Egyptian jatropha seeds for extraction of oil. Optimum oil yield was found to depend on temperature, time, motor power and torque. The favorable
conditions for maximum oil extraction from Egyptian jatropha were reported as 100°C and 60 rpm. It was also reported that, operation of screw press beyond 100°C has increased the free fatty acid levels in the extracted oil. A comparative study on the oil extraction capacity and oil quality from wild apricot kernel by Kate et al [56] was reported as: oil extraction by means of traditional manual kneading was laborious and required repeated processing of the same paste. Also, extraction was found to be not complete and wastage of oil was noticed. Whereas, with motor driven expellers, oil quality was improved due to decorticators at less labor requirement and has a throughput of 150kg/hr. The firm has concluded that wild apricot kernel extraction by expeller press has high efficiency than the traditional manual kneading method. In another study, optimization of mechanical extraction of *Jatropha curcas* seed was studied and the effects of temperature, rotational speed of screw press and press cylinder size on chemical properties of jatropha oil to be used as stove combustion fuel were reported. Optimum operation of screw press was found based on oil recovery, analyzing time and residual oil in the seed cake. The optimum conditions for jatropha seeds were reported as 260 rpm and press with 1mm holes [57]. A comparative oil extraction study was carried out with Australian native beauty leafs seed (*Calophyllum inophyllum*). Oil extraction was carried out with electrically driven screw press and n-hexane solvent extraction. The results have shown that the oil can be extracted by screw press at low cost but higher yields can be obtained with solvent extraction [58]. Algal oil extraction was carried out with mechanical expeller and hexane solvent extraction. Solvent extraction has recovered the oil completely from the algae, leaving 0.5%-0.7% in the residue whereas, only 75% of oil recovery was reported with expeller method. It was demonstrated from the study that, solvent extraction can be an effective method for the oil extraction from algae but has the disadvantage of high cost [59]. Ali et al [34] have conducted a comparative study on the extraction of oil from flax seeds by mechanical expeller, solvent extraction, microwave assisted, ultrasonic assisted and combine microwave and ultrasonic assisted extractions. The maximum oil yields on % weight basis were obtained as 22.6%, 36.3%, 10%, 42% and 27.8% respectively. The relative ratios of energy consumption were calculated based on the energy requirement and energy recovered from each process. Net energy ratio was found to be highest 25.21% for microwave assisted extraction and thereby concluded that microwave assisted extraction is an efficient and energy feasible method to extract oil from flax seeds. The extraction efficiencies of microwave assisted extraction and ultrasonic extraction were compared with conventional solvent extraction for soybeans using different solvents such as hexane, isopropanol and mixture of both. It was found that the extraction yields were high for both ultrasonic assisted and microwave assisted extractions in mixed solvent of hexane and isopropanol [60].

5. Conclusion:

The efficiency of oil/lipid/fat extraction depends on the method adopted and the material source. Mechanical methods have advantages of producing high quality oil. Solvent processes reduce the extraction time and mechanical wave based systems are capable of increasing the efficiency as well as yield of extraction. The other side, each method has its own drawbacks. The process of extraction for biofuel production has experienced a tremendous change and in particular advancements with the development of unconventional extraction techniques such as ultrasonication, microwave and supercritical fluid extraction techniques. However, the limitations associated with these techniques still demands further research in the field to satiate the alternate fuel energy needs.

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