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Applications of Waste Cooking Oil Other Than Biodiesel: A Review

D. C. Panadare, V. K. Rathod* [*]

Department of Chemical Engineering, Institute of Chemical Technology, Mumbai, India

Abstract

Waste cooking oil (WCO) is being generated large scale all over the world; hence it has devised serious problems of its waste management. Organised collection of WCO in voluminous quantity is mainly used for the production of biodiesel. Most researchers focus primarily on the biodiesel generation from WCO, although other applications are also important and require attention. Objective of this review article is to highlight most of the aforementioned possible applications of WCO which may help in its utilization apart from biodiesel. It can be processed to obtain pyrolytic oil, hydrogen gas, biodiesel or electricity production by direct burning. Applications like combined heat and power generation (CHP) can utilize WCO with utmost efficiently. It can also be processed chemically to obtained biodegradable polyurethane sheets, greases, biolubricants, soaps and alkyd resins. Properly purified and sterilized WCO can be used as a carbon source in fermentation processes for the production of rhamnolipid biosurfactant and polyhydroxybutyrate (PHB). Waste cooking oil therefore can be considered as a potential waste which can be utilized as energy source and raw material for chemical or biological processes.

Keywords: *Waste Cooking Oil (WCO), Combined Heat and Power (CHP), Pyrolytic Oil, Hydrogen*

1. Introduction

Advancements in the field of science and technology have led to great innovations in various fields, which have also created serious problems of pollution such as emissions of harmful gaseous, disposal problems of the hazardous industrial wastes as well as household waste in gaseous, solid or liquid forms. Production of useful products or energy production is the latest approach for efficient waste management and utilisation of waste products across the globe. More specifically petroleum based products are becoming more costly and are nonrenewable, hence more focus is given on the products development for their replacement [1]. Increasing population leads to increase in the demand of food items such as grains, vegetables, milk and milk products, cooking oil which also leads to generation of kitchen waste. Among these kitchen generated wastes, WCO and fat have created serious problems for their disposal due to its slow degradation. All over the world,

∗ Corresponding author: vk.rathod@ictmumbai.edu.in

cooking oil is one the most essential components in food preparation. Cooking oil is used in substantial quantity for food frying either in home, restaurants or in Food Industry. During the frying process, oil undergoes many physical and chemical changes. These changes after prolonged cooking make the oil unfit for human consumption. It may cause serious health hazards, such as potential gastrointestinal disorders and even mutagenesis in the human body. Physio-chemical changes that occur in cooking oil mainly include, change in colour, odour, viscosity, calories count [2]. It also contains particulate matter and increased amount of total polar solids, polymeric molecules as it undergoes chemical reactions [3] as mentioned in Table 1.

Waste cooking oil causes some serious environmental problems including bad odour. It is said that one litre of oil poured into natural waters may pollute 500,000 L of water. Mainly it increases the organic load on water bodies and also forms a thin layer over water that reduces required dissolved oxygen concentration for underwater living creatures [4]. Waste cooking oil disposed incorrectly in to the kitchen sinks can solidify and hence block the sewer pipes. Further degradation of WCO in pipes may also cause corrosion of metal and concrete elements [5]. Thus removal of WCO from sewer streams at sewage treatment plant adds extra cost to it [4]. Generally it is separated by using grease traps from sewage lines or near effluent treatment processes (ETP) along with other organic matter and digested in an anaerobic way to obtain biogas (specifically methane) [6]. Waste cooking oil or grease can be collected before it discharges into the sewer,which is more efficient for governments in treating effluents [7]. Free fatty acid (FFA) content of WCO is very high as compared to normal cooking oil. If FFA in cooking oil is less than 15% it is said as yellow grace otherwise named as brown grace (15-60% FFA by weight) which has much greater viscosity. Proper waste management is thus necessary for WCO to overcome problems [3].

Table 1
Chemical changes occur in WCO during the process of frying.

Sr. No.	Chemical Reactions	Reaction Cause	Change in Chemical Composition
1	Hydrolysis	Water content in the food interacts with frying oil at high temperature, reaction with atmospheric moisture	Increase in concentration of total polar molecules, production of free fatty acids, glycerol
2	Thermal Degradation	Triglyceride degradation at high temperature in absence of oxygen	Produces alkanes, alkenes, symmetric ketones, oxopropyl esters, CO, and CO_2, dimeric compounds
3	Oxidation	Reaction with surrounding atmospheric air/ oxygen.	Hydroperoxide formation, change in content of conjugated dienes and trienes.
4	Polymerisation	Reactions with in unsaturated fatty acyl groups at high temperature	Formation of polymerised triacylglycerides (PTG) Including dimers and oligomers.

Waste cooking oil is generated on large scale by restaurants due to deep fryers. According to the Energy Information Administration in the United States capita, about 378 million L of WCO can be generated in USA per day. Canada, European countries and the UK are reported to produce approximately 135000, 700,000-1,000,000 and 200,000 tons per year of WCO respectively [8]. Countries with larger populations like China and India also produce large amounts of WCO. China generates about 4.5 million tons WCO per year. In India, the exact amount of WCO generated is not available but according to 2009−2010 oil consumption configuration about 0.167 million tons of WCO can be predicted. Japan and Ireland produce about 0.45−0.57 and **0.**153 million tons of WCO per year [9]. Such huge production of WCO in the world creates problem of its collection, treatment and disposal.

In many countries like the USA and Japan laws regarding WCO disposal are very strict. There are many private companies which usually collect the WCO and process it mainly for biodiesel production or even electricity production. Kumar Plocher use WCO collected from restaurants to produce about 1.9 million L of biodiesel per year [7]. Waste management system for WCO capable of utilizing radio frequency identification (RFID) also helps in waste management. Such system mainly deals with logistics, cash flow and information flow. Collection of Waste Oils (WO) from restaurants, houses, street venders followed by its qualitative and quantitative analysis, storage, transportation, processing, distribution of end product according to market value are done by such systems. Analysis of proper statistical records with such systems may provide the option of profitable waste management [10].

Systematic disposal of WCO from fryers to storage tank is necessary as it serves a major source of WCO. It is usually done by manual handling. Researchers have designed a better option to transfer the WCO from deep fryers directly to the storage tank. Most of the systems that include potable device for WCO transfer are patented. These patented systems include parts such as tubing as carrier of WCO, handy pumping system (helical pump), and control panels [11]. Some systems also mentioned specialized containers used for storing, transferring and transporting WCO which mainly involve input pump with internal grinder and timer, heating coil to maintain inside temperature so as to keep oil in liquid state and indicator lights to notify operator when tank is full, near to tank capacity [12,13]. Initially in 1993, a patent was filed for the distribution of cooking oil and removal of system WCO from deep fryers. The system included filter, waste, supply, and fryer stations with proper tubing to assemble all parts and carry oil, valves, safety sensing device [14]. Regular practice of such systems for places where deep fryers are regularly used may provide safe, easy and greener route of transport and disposal of WCO. In the process of frying, fresh cooking oil undergoes many undesirable physio-chemical changes that ultimately restrict its further utilisation. Thus characterization of WCO is mandatory for a scientist before actual experimentation of its processing. Analysis of different properties of WCO such as acid value, viscosity, fatty acid profile, calorific value showed remarkable diversity in values depending upon its source and way of utilisation. Ways of utilising cooking oil always differ in cooking time, cooking temperature and food items cooked. Practice of cooking oil utilisation also varies on large scale for household cooking and restaurant cooking such as fast food, casual or fine dining, etc. Detailed analysis of WCO collected from 16 local restaurants for fatty acid profile, acid value and dynamic viscosity was done by Knothe *et al*. [15]. Their observation showed that WCO undergoes process of hydrogenation and oxidative degradation during cooking or frying which is responsible for changing its properties. As WCO follows non-Newtonian behaviour (pseudoplastic-dilatant) its kinematic viscosity needs to be checked with rotational-type viscometer for consistent behaviour and found to be increased as that of the unprocessed oil. Author observed increase in the saturation level, i.e. increase in mainly saturated and C18:1 (monounsaturated) fatty acid chains and decrease in C18:2 content by 6.57% on average. While acid value and dynamic viscosity analysis showed average increase of 4.02 and 7.46 cP respectively. Values regarding physio-chemical properties of WCO on analysis show large deviation, but according to the author they cannot be linked to its fatty acid content. Besides, analysis of other factors such as moisture content, carbon content is also necessary before application of WCO as a raw material in any process. Khalisanniet [16], worked on the detailed analysis of WCO collected from a hotel at Teknologi MARA University campus where they observed that WCO contains an average 0.02% moisture, 0.003% ash and about 99.919% fixed carbon. Heavy metals such as Cr, Ni, Pb were absent while Cd was present at about 0.041ppm. Calorific value of WCO was found to be 38.314 MJ per kg which was observed to be higher than unused cooking oil, i.e. approximately 14MJ per kg. This detailed analysis helped the author to conclude that WCO can be a good source of energy [16]. Systems for continuous monitoring of total polar molecules during the process of frying were also developed to declare the point where edible oil turns to WCO [17]. Most of the parameters that need to be analysed before processing of WCO can be listed as in Table 2.

Large deviation in the characteristic values of WCO is unsuitable for its direct use in any process. Therefore cleaning or partial purification of cooking oil before further application can be done by various physical and chemical methods like filtration, adsorption, chromatographic techniques, and extraction by solvents, etc. Amendment of such systems include systematic use of filter screen, low positive pressure pump followed by filter pad, which consists of activated charcoal held together by a resin binder, along with pressure sensors [21]. Settling treatment at ambient temperatures can also be applied to WCO to separate sludge fraction from an oil fraction. It mainly includes gravity based settling or mechanical settling like centrifugation [22]. Chromatographic techniques with combination of gel-derived alumina, activated clay, magnesium silicate were found to be efficient in removing free fatty acids to a greater extent and also improve

Table 2
Analytical Parameters, Approximate Values and their Methods for Unused cooking oil (UCO) and Waste cooking oil (WCO).

Sr.no.	Parameter to be analysed	Method of analysis used	References
1	Ash content	Temperature 550°C for 4 h to determine the ash matter) Content.	16
2	Moisture content	Heated in the oven at 100-110°C for 10 min to remove the moisture	16
3	Polymerised triacylglyceride (PTG)	Gel permeation chromatography (GPC) , near infrared (NIR) spectroscopy, Partial Least Squares (PLS) regression	18
4	Heavy metal content	AAS	16
5	Fatty acid analysis	Gas chromatography	19
6	Peroxide value	Modified iodometric method	19
7	Content of conjugated dienes (CD) and trienes (CT).	Spectrophotometer	19
8	Acid value	Titration	16
9	Viscosity	Cone and Plate Viscometer	18
10	Total polar molecules (TPM)	TLC, Gravimetrically with by silica column chromatography following IUPAC	20
11	Colour	Reflectance Colorimeter	20
12	Dynamic interfacial tension	BPT-1 tensiometer	18
13	Density	TD1 tensiometer	18

colour and odour of WCO, without soap formation [23]. Moisture removal from WCO can be done by vacuum filtration [24]. Deacidification of WCO, if needed, can be performed by various methods like neutralization with alkaline solution, esterification with glycerine, extraction by solvents like ethanol, distillation of fatty acids, ion-exchange chromatography [24].

Clean WCO, nowadays is sold to the market by various companies at determined market price. Although most WCO generated is utilized by companies for the production of biodiesel, there are many applications of WCO which are not yet exploited commercially large scale compared to biodiesel. Earlier most review articles discussed utilization of WCO for biodiesel production, different catalysts used [2], process intensification methods [9] and economic and environment values [3]. However, there are many other applications of WCO that are not considered by these review papers. WCO can be used as a source of energy for various other applications such as hydrogen gas production, pyrolytic oil production, electricity generation. Some chemical processes may also convert WCO to commercially important products such as bio-lubricants, graces, resins, biodegradable polymers. Such applications of WCO, other than Biodiesel production need to be focused for maximum research and commercial applications. Thus, the main focus of this review is to enlist the most possible applications of WCO which can be applied on household, small or even large scale.

2. Applications of waste cooking oil

2-1. Waste cooking oil as source of energy

Sustainable production methods of new generation fuels such as bio-fuels and hydrogen are now more intentionally studied from the view of reducing greenhouse gas emissions. Concept of waste-to-energy is now growing tremendously due to rapid depletion of fossil fuels. Alternative fuels which are mostly under the concept of waste-to-energy generally uses raw material like agricultural waste or different types of used or waste oils such as WCO or waste lubricating oil, used transformer oil, used engine or gear oil [25]. Products generated such as biodiesel, bio methanol, hydrogen gas, H_2/CO, low molecular weight hydrocarbons including methane using WCO make it a potential raw material for energy generation. These products can further be used to produce electricity or to run vehicle or machines. Thus energy generation from WCO can be considered as an effective technique for waste management, as well as a beneficial form of energy recovery. Rudolph Diesel [26] first demonstrated that vegetable oils could be used as a fuel to run engines. But some properties of WCO such as low volatility, reactivity of unsaturated molecules, high viscosity, high acid value and contamination by food particles, cause problems such as blocking injectors, carbon deposits [27]. Some methods are used to improve the properties of WCO so that it can be further used as a source of energy such as dilution with diesel fuel or solvents, micro-emulsification, transesterification, pyrolysis [28]. Conventional method of WCO utilisation includes collection of WCO with burnable garbage that are burned together by a combustion process that produces a heat stream for the purpose of generating electricity using a stream turbine. This method has drawbacks such as residual ash production, disposal of residual ash and emission of harmful gases. Small scale, WCO can be combusted to generate flame, which can also be used for heating purposes. This property can be exploited to application such as burner with great market potential. That may consist of provision for WCO to be partially separated from its contaminants and selectively entered to burner with different flow rates. Also, small appliances like lawn mower, boilers running directly on WCO are available in the market [29]. Recent applications such as pyrolysis, hydrogen loop reforming or combined heat and power system, have thus been a topic of interest for research and thus are discussed in the following sections.

2-1-1. Pyrolysis of WCO

Pyrolysis is a thermo cracking process, simply called thermo chemical reaction where high temperature is applied in limited amount of oxygen which produces various gasses, liquids and solids. Pyrolysis of used frying oil composed mainly of linoleic, oleic, palmitic and stearic acids as triglycerides was studied by Dandik and Aksoy [30] at different temperatures (400°C to 420°C) for about 180 min. Experiments were performed with fractionating columns having 180, 360, and 540 mm length. Products obtained after pyrolysis were mainly condensable hydrocarbons like C5-C17 paraffin’s, olefins. Aromatics, cycloparaffin, cycloolefins and gases like H_2, CO, CO_2 were also obtained in small quantities. The authors also observed that increasing temperature and decreasing length of columns gave increased reactant mixture conversion. Where olefin fraction obtained was more at elevated temperature. Thus liquid hydrocarbon product obtained in high concentration can be used as fuel as they are in gasoline boiling range. Dandik and Aksoy [30] studied pyrolysis of used sunflower oil in presence of catalyst like sodium carbonate, silica–alumina, and HZSM-5. Authors observed the highest conversion of 73.17 wt% with sodium carbonate as a catalyst.

Francis Billaud [31] reported the pyrolysis of WCO (VEGETAMIXOIL®) to produce H_2 or H_2/CO, low molecular weight gaseous hydrocarbons(C1-C4), high molecular weight hydrocarbons (linear 1-olefins and n-paraffin's) and coke which can be further used as a source of energy in a fuel cell or helped in biodiesel production in Fischer-Tropsch catalysis ($H_2/CO=2$) or bio methanol production $(H_2-CO_2)/(CO+CO_2)=2$ or can be used as raw material in further chemical processing. Steps followed by the author are given in Fig. 1. Author also found that coke is rapidly consumed by water to form hydrogen and carbon monoxide as stated below.

$$C + 2H_2O \rightleftarrows CO_2 + 2H_2$$

Author also mentioned that addition of water promotes light hydrocarbon formation whereas formation of CO, CO_2 and H_2 is higher at 800°C than at 700°C. Amongst the two diluents, i.e. pure water and equimolar mixture of water and nitrogen used by the author, pure water steam was found to be efficient. It is also mentioned that the reduction in the residence time by half can be done by adjusting flow rate of WCO. Reaction inhibitor (thiophene) added in the mixture up to 300 ppm will lead to decrease in CO and CO_2 up to 6.3% and 5.4% respectively.

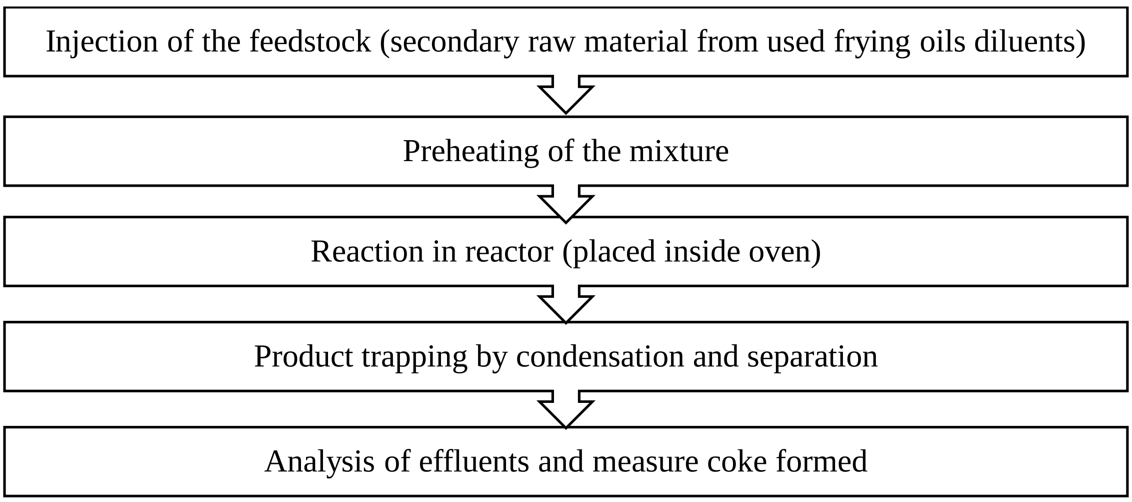

Figure 1. Steps for pyrolysis of Waste Cooking Oil.

Singhabhandhu and Tezuka [32] studied waste management regarding waste plastic (WP), waste lubricating oil (WLO) and waste cooking oil (WCO). Normal waste management practice in Japan includes combustion of WCO (collected with other burnable garbage) and WLO together to produce steam heat which is then used for generating electricity by a steam turbine. This traditional method of waste management was compared by authors with another system where pyrolytic oil is generated in combination of WP, WCO and WLO in four systems. Results obtained by authors are mentioned in Table 3. Authors suggested that combined use of WCO, WLO and WP for generation of pyrolytic oil can be the best economic and energy efficient practice. This pyrolytic oil has been considered as a biofuel with low greenhouse gas emission. It can be commercially used as energy source in turbines, boilers, also in engines, and considered as an economic and high hydrocarbon containing fuel [33]. Pyrolytic oil can be considered as efficient substitute for both heavy and light fuel oils and used to run internal combustion diesel engines, gas turbines, boilers, furnaces, and turbines for electricity. The heating value of pyrolytic oil was about 93% of heating value of diesel [32] with flash point (80°C) which is more than biodiesel. Pyrolytic oil also has lower nitrogen oxides and almost no sulphur and hence form less smog and no corrosion problems.

2-1-2. Hydrogen gas production from WCO

Hydrogen gas can also be efficiently produced from WCO by steam reforming process with packed bed column which is a more

Efficient method than catalytic reforming where complete conversion of oil does not occur [34]. Process of unmixed steam reforming can also be coupled with in situ CO_2 sorption adsorbent within the reformer [35]. These methods can produce a nearly pure stream of hydrogen. Unmixed reforming combustion process mainly consists of alternative input of air and mixture of fuel and steam over the packed bed of catalyst. Nickel was observed to be a better catalyst to undergo oxidation reduction process for alternate passing of air and fuel. Steps followed in unmixed reforming [36] can be described as in Fig. 2.

Table 3

Pyrolytic oil generation from waste with cost estimation.

Raw material used	Maximum Yield of pyrolytic oil (ML/y)	Average Unit Production Cost (USD/L)
WCO +WP	4.91	0.31
WCO +WLO	35.57	0.25
WLO +WP	36.63	0.24
WCO + WLO + WP	38.03	0.24

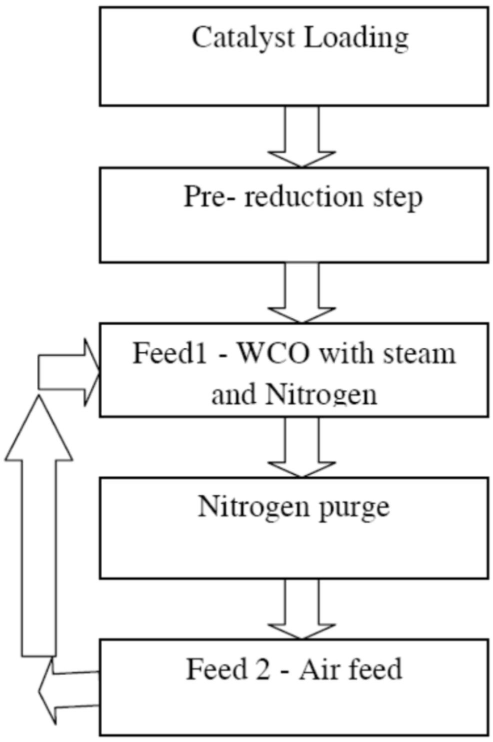

Figure 2. Steps for Hydrogen-reforming process of waste cooking oil.

Pimenidou *et al*. [36] studied chemical loop reforming of WCO with packed bed reactor within the temperature range of 600 to 700^{0}C at 1 atm. The same system was also studied with CO_2 sorbent (pre-calcined dolomite) loaded at the centre of the reactor by the same author. Six cycles of air and fuel-stem resulted in about 100% hydrogen purity in first pass followed by about 95% purity in the following five cycles with carbonation efficiency stabilized around 56%.

Reaction scheme in the steam loop reforming of WCO can be mentioned as shown below:

1) For steam-WCO feed

1.1 Catalyst reduction by WCO

$$C_nH_mO_k + (2n + 0.5m - k)NiO \rightarrow nCO_2 + 0.5mH_2O + (2n + 0.5m - k)Ni$$

1.2 Steam reforming

$$C_nH_mO_k + (n - k)H_2O \rightarrow nCO_2 + (2n + 0.5m - k)H_2$$

1.3 Water gas shift reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

2) For Air feed

2.1 Gasification of Carbonaceous deposit

$$C + O_2 \rightarrow CO_2$$

$$C + 0.5O_2 \rightarrow CO$$

2.2 Oxidation of catalyst

$$Ni + 0.5O_2 \rightarrow NiO$$

Thus Steam loop reforming system with dolomite can be an efficient and green method for utilizing WCO to generate hydrogen gas successfully.

2-1-3. Transesterification of WCO

The most common and industrially accepted application of WCO is production of biodiesel that is mono alkyl esters of long-chain fatty acids obtained by the process of transesterification. Biodiesel exhibits many advantages such as renewability, domestic origin, environmental benefits in terms of biodegradability and reduction of most regulated exhaust emissions, safer handling due to higher flash point, and inherent lubricant [37]. Triglycerides from WCO react with alcohol in presence of catalyst which may be acidic, basic or enzymatic in one of two steps of the process to produce Fatty acid methyl ester (FAME) that is biodiesel along with glycerol as by-product. Biodiesel obtained is generally used as blend with diesel to run generators or vehicles [38]. Cost analysis of biodiesel production highlights that the major cost of production is added by the source of raw material used for production [39]. Initially, vegetable oils used as raw material make the process cost inefficient. Use of WCO thus solved this problem to a certain extent. Authors have calculated biodiesel production from collectable WCO in Iran which costs up to 1.201$ per L of biodiesel whereas gross production value of biodiesel was observed to be about 2.499$ per L [40].

Novel work is now done in finding green methods for biodiesel production such as use of green solvents like Dimethyl carbonate (DMC), use of enzymatic catalysts [39], etc. Biodiesel production was also done by using whole cell biocatalyst, where Rhizopus oryzae PTCC5174 immobilised on polyurathene based biomass supported particle was used as catalyst. This green catalysis was observed to give about 88% conversion, when provided with proper pre-treatment to WCO such as filtration and heating [41]. Process intensification for biodiesel production by applying hydrodynamic cavitations [42], ultrasound [43] technology is now intentionally studied by scientists to have maximum conversion in less time. Experimentation done separately by scientists revealed that about 95% and 93.5% conversion of WCO can be done in 10 min and 30 min respectively by applying hydrodynamic cavitations [42] and ultrasonication [43] differently. Biodiesel generated by using WCO was tested on diesel engines to run generators as well as vehicles. It was observed that 100% biodiesel as well as its blend with other fuel (petroleum diesel) can be successfully used as clean fuel [37]. Biodiesel will always be the most desirable application of WCO, although not all WCO generated worldwide is converted to it.

2-1-4. Ozone treated oil

It is always a topic of interest for researchers for generating high efficient fuel from WCO which can be directly taken up by diesel engines. Ozone treated oil can thus be obtained from WCO after the treatment of preheated WCO with water and/or ozone. Resulting fuel from the patented method and equipment have shown higher calorific value (about 9730 kcal per kg), lower ignition point (about 51.3^{o}C) and lesser density than the conventional biodiesel formation. Fuel obtained by the process can thus be economic and an efficient substitute of traditional methyl ester production [44]. There is little scope for scientists in the field of ozonation of WCO, process intensification and its market potential.

2-1-5. Electricity generation from WCO

2-1-5-1. Combined heat and power (CHP) system

Combined heat and power (CHP) System is one of the promising applications of WCO in which electricity is generated from WCO. Also, heat produced during the process can also be utilized for other purposes like heating water. The process is based upon Organic Rankine Cycle where both liquid and gaseous phases are involved [45]. System mainly consists of parts like WCO reservoir tank, Filtration units, Combustion unit, Expansion unit, Generator unit, Pumping unit, Condensing units, Exhaus unit. There are commercial products available in markets based upon this system. Vegawatt™ is one of the prime products of Owl Power Company which is an automated CHP system that was awarded as one of the Popular Sciences 2009 Invention Awards [46].

CHP system along with WCO can utilize different types of fuel such as biomass, bio-oil, vegetable oil, fats, thus it can be a good alternative for petroleum based fuel. Availability of fully automated CHP equipment on different scale (local to global scale) makes this technology more versatile [47]. As the system can directly take up WCO as its feedstock and in return gives hot water and electricity as its output, makes it quite efficient to restaurants using deep fryers. Micro-scale designed for processing WCO is about the size of a refrigerator. Fully automated CHP for WCO processing which are available in the market generally have a Sensory system [48] as shown in Fig. 3.

The system is said to capture about 70% of the fuel's calorific value as CHP is a cogeneration process where heat generated by fuel after combustion is not released in the atmosphere, instead it is utilized for hot water or steam production in the premises [49]. Commercial systems available in the market can provide different ranges of electricity generation unit from 4kW to 12 kW where the amount of waste vegetable oil consumed per week for these units is about 114-454 L. The process is considered as greener since emission of toxic gases like NO_x, SO_x, and CO_2 are much less than that of other fuels used [50]. For the production of 1 kW electricity CO_2 emission by coal, Fuel-oil (petroleum diesel), Natural-Gas-fired electricity generator and WCO in CHP releases approximately about 1016, 988, 670 and 642 g of CO_2 respectively. The process does not require any catalyst and reduces dependence on fossil fuels.

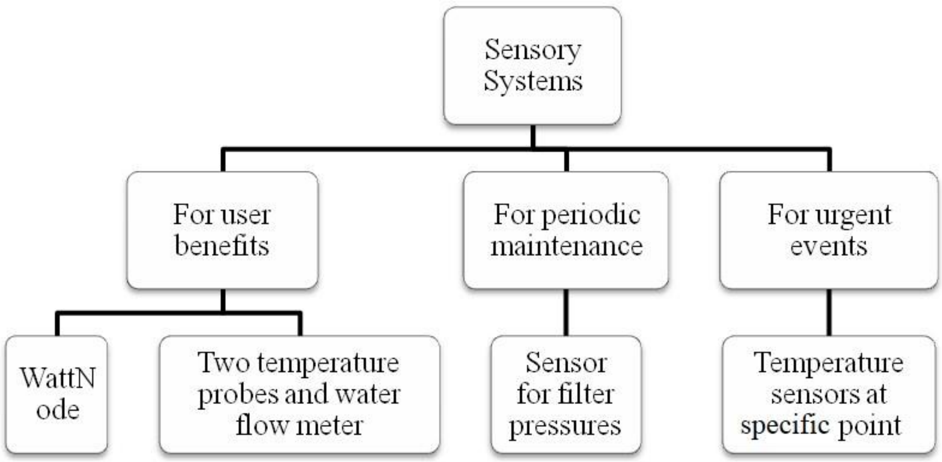

Figure 3. Sensory system needed for combined heat and power system.

2-1-5-2 Electric generators coupled with external combustion steam engine

Another way of generating electricity from WCO is use of electric generators coupled with external combustion steam engine. Patented technology provide a compact device which is able to generate high kilowatt with reduced emission of nitrogen and sulphur oxides. Technology involves combustion of filtered WCO fuel that generates heat which is further used to produce steam. Steam is then used to rotate electric motor coupled to electric panel, generating electricity [51]. Such technology can bring revolutionary change in future which helps in reducing dependency of human beings on fossil fuel. Waste cooking oil utilization with this application can be studied further, as the reported in literature related to this topic is less available.

2-1-6 WCO as fuel in internal combustion engines

Waste cooking oil free from particulate matter can be directly used as a fuel in internal combustion engines like diesel engines. Waste cooking oil as a fuel can provide better power output about 313 kW than other fuels like red diesel, rape seed oil, soya oil, sunflower oil or even biodiesel used under the same conditions. Also, power output obtained was observed to be comparatively clean as it reduces the emissions of sulphur oxide (<0.001 mg per L), nitrogen oxide (1.491 mg per L), carbon monoxide (1.328 mg per L) and particulate matter (0.035 mg per L) at normal temperature and pressure [22].

2-2. WCO as fermentation media component

Huge amount of generation of WCO has created a problem for its disposal. Biodiesel production from WCO can be one of the best alternatives for its efficient utilization. However, the processing cost of biodiesel production from WCO is high which makes the product costly. Thus utilisation of WCO for the cost efficient production of value added products needs to be studied. Most researches have successfully screened microorganisms which can accumulate surface active compounds by utilising WCO as a potential carbon source in the process of fermentation [52,53]. Due to availability of large amount WCO as a waste material, reduction in the production cost of fermentation product can be achieved. Thus, WCO used as a feed stock in biotechnological processes makes the processes economical and in some cases gives a higher yield [54] than previously used carbon sources such as glucose. Almost all oils used in the fermentations were sterilized separately before being added to media. Sterilization can be done by steam autoclave. Waste cooking oil added in most of cases was filtered but in some cases it was added without filtration [55]. Waste cooking oil used as a fermentative media should always be checked with chemical properties like the percentage of saturated and unsaturated fatty acids, moisture content, free acidity, peroxide number, presence of particulate matter (for filtration step determination) [56].

Bio surfactants and bio emulsifier’s production are high cost processes with low yield. The type of carbon substrate used as a substrate influenced quality as well as quantity of these biomolecules. Waste cooking oil was used as basic media components for production of these biomolecules with reduced production cost and increased yield. Different strains of *Pseudomona aeruginosa* strains like L2-1, B1-3, 7a, 6c were checked for the fermentative production of rhamnolipids and polyhydroxyalkanoates (PHA's), where substrates like Glycerol, WCO, cassava wastewater (CW) and combination of cassava waste water with WCO were used [57]. Among all strains tested with different substrates, the highest biomass was obtained with WCO by *P. aeruginosa* 7a strain (6.8 g per L). Also, among all substrates, all strains gave the best results for WCO as a substrate in terms of PHA production, with between 43 and 50.4% PHA of the dry weight. Waste cooking oil as carbon source showed 4.2 g per L dry cell mass for strain L2-1 along with PHAs production of 39% of cell dry weight. Produced PHAs have chain length between C8 and C16 and the unsaturation level of the monomers showing considerable variation as per the carbon source used. When WCO was used as carbon source, an increase in content of unsaturated monomers (4.8%) and short chain monomers (C8:0-37.5%, C10:0–42.1%, C12:0-13.2%) was observed for the same product. Thus WCO, being a hydrophobic substrate gave higher yields of PHA than hydrophilic substrates such as glycerol. Rhamnolipids are the products obtained by the same fermentation process, where WCO gave a more constant yield, varying between 245.6 and 273.1 mg per L. The dirhamnolipid RhaRhaC10C10 was predominant except for WCO, where the monorhamnolipid are dominant. Production of unsaturated rhamnolipids is similar and did not vary as per carbon source. The author also concluded that hydrophilic substrates, such as sugars, were assimilated more rapidly than hydrophobic or oil as a carbon source [57]. For the uptake of oil in the form of bioavailable fatty acids and glycerol by microbes, WCO should be enzymatically degraded. Strain L2-1 was found to produce lipases and esterases in presence of WCO or CWO as a media component that degrades triglycerides. In continuation of the same fermentation process, after stationary growth phase has been reached, production of rhamnolipids (biosurfactant) was observed. Biosurfactant formed also helps in solubilising the considerable amount of residual oil still present after 72 h. Simultaneous production of PHAs and Rhamnolipids makes the process more economic.

George [58] in 2012 studied production of extracellular rhamnolipid biosurfactant from six Pseudomonas strains isolated from oil samples near a coconut oil mill in India and *P. aeruginosa* MTCC 2297. When waste coconut oil was used as substrate all strains were observed to produce rhamnolipids (Rha-Rha-C10-C10, Rha-C12-C10 and Rha-C10-C8/Rha-C8-C10). Optimised process for 7 days with one of the screened strains mentioned as *P. aeruginosa* D by author was found to give highest rhamnolipids production of 3.55 g per L and emulsifying activity of 71.7% which was greater than the yield obtained by using normal coconut oil.

Cooper and Paddock's medium is a widely studied media for some fermentation processes [59]. This media consists of WCO along with glucose in different concentrations along with 0.1% KH_2PO_4, 0.5% $MgSO_4 \cdot 7H_2O$, 0.01% $CaCl_2$, 0.01% NaCl, 0.5% yeast extract. Concentration of WCO and technical grade glucose varies from 1 to 10% and requires experimental optimization which varies with different fermentation processes. Generally, 5% WCO and 7 to 8% technical grade glucose is used. Various strains of *Saccharomyces cerevisiae* strains were observed to have potential to produce biosurfactant. Cooper and Paddock's medium when used for these strains for biosurfactant production showed that Y42 yeast produced the highest biomass up to 20.01 g per L while *S. coreanus* 2023 produced the lowest biomass of 4.35 g per L. This media consists of about 8% glucose and 5% WCO. Optimised concentration for this particular fermentation process was 5% glucose and 5% WCP which gave high biomass production and emulsification activity too. It was observed that WCO was utilized by *S. cerevisiae* 2031 as additional carbon source for biomass production but, consumption rate of WCO was reduced with time [59]. Maximum uptake observed by author is 37.58% till day six. Presence of water–immiscible substrate triggered the biosurfactant production after consumption of soluble competitive metabolite.

Cupriavidus necator was a well-studied source for the production of polyhydroxybutyrate (PHB). Pure rapeseed oil, heated rapeseed oil and waste frying rapeseed oil were used by Verlinden *et al*. as media components to study fermentation system [55]. Use of WCO gave PHB yield of 1.2 g per L, which is similar to yield obtained by glucose. Whereas pure oil and heated oil were used produce 0.62 g per L and 0.9 g per L of PHB respectively after 72 h. It was observed that saturated fatty acids lead to build-up of more energy-rich PHB as compared to unsaturated fatty acids. The same strain *C. necator* H16 and its transformed mutant, *C. necator* PHB4 when used for the production of PHA, obtained excellent results with WCO as carbon source and urea as nitrogen source [60].

Not only biopolymers and surfactants but also some essential enzymes and biomolecules were produced by scientists using WCO as an essential component of substrate. Papanikolaou *et al*. [56] studied the fungus like *Aspergillus* and *Penicillium* strains which can utilize WCO for fermentative production of extracellular metabolites (organic acids) and enzyme (lipase) and the substrate fatty acid along with lipid rich biomass. Waste cooking olive oil, obtained from a local restaurant facility was used by the author which resulted in biomass quantity produced up to 18 g per L. Lipid accumulation by *Aspergillus* was about 64 (w/w% of dry fungal mass) along with extracellular lipase with maximum activity of 645 U per mL as well as oxalic acid up to 5.0 g per L. Waste cooking oil as a pollutant when studied with biodegradation point of view using *Yarrowia lipolytica* CECT 1240 strain resulted in excellent results. Author reported about a 90% decrease in COD when fermentation was carried out in bioreactor in a time period of 3 days. In the same process, addition of WCO was used for the excess production of extracellular lipase by the organism [61]. Riboflavin, most commonly known as vitamin B2, is an essential component of human consumption. Study of fermentative production of riboflavin using *Ashbya gossypii* strain was observed to utilize a variety of carbon sources including soybean oil and corn oil. Researchers have successfully used WCO as carbon source for riboflavin production. About 40 gm per L of WCO used in media give maximum riboflavin production of 6.76 g per L after optimising other parameters like pH [52].

2-3. Waste cooking oil as raw material for value added products

Chemical composition of WCO mainly consists of triglycerides as well as a considerable quantity of free fatty acid. Many chemical or enzymatic processes can successfully utilize WCO for the production of new chemical entities as value added product. In the process of formation of biodiesel from WCO, considerable amount of glycerol is also generated which can be further used for different purposes. Glycerol obtained can be used as is for production of hydrogen gas, methanol, low grade animal food and chemicals (polyethylene glycol) as well as in effluent systems. Whereas glycerol obtained can be purified and supplied to other pharmaceutical, food, textile and chemical industries as raw material [62]. Major contaminants observed in the glycerol obtained during biodiesel production are inorganic salts, free fatty acids, catalysts used for transesterification reactions. Thus, by adding strong sulphuric acid glycerol can be purified [63].

2-3-1 Application of WCO for grease preparation

Grease has a wide scope of application in the field of machines as it is used to minimise the friction between mechanical parts. Grease are mostly developed from petroleum based raw materials but are non-biodegradable. Abdulbari and team [64] worked on an eco-friendly option for grease especially derived from waste materials like WCO and spent bleaching earth. Thermal degradation of cooking oil produces polymeric impurities after reacting with water. Thus WCO possesses inherent viscosity, higher flash and fire points. Also, it is biodegradable easily available waste material and so used as one of the components in grease production. Grease from waste cooking oil was prepared by vigorous mixing of WCO and SBE at room temperature about 21^{o}C by an ove head stirrer. Different formulations tested with 20 to 50% of WCO balanced by SBE concluded that formulation containing 70-75% SBE balanced by WCO was more desirable. Grease formed with this combination was stored for prolonged time period (more than one month) resulting in to migration of oil from the thickener and as such a change in consistency. The author has recommended a detailed study on the same topic like the addition of antioxidants to avoid oxidation of WCO.

2-3-2. Application of WCO for synthesis of bio lubricant

Another value added product developed from waste cooking oil is ‘bio lubricant’ (octyl esters). Most of the lubricants available in the market are petroleum based, hence the need for an alternative economic and ecofriendly source. Scientists have developed bio lubricant from virgin vegetable oils such as soya bean oil, castor oil, rapeseed oil, palm oil, jatropha oil, etc. In the case of bio lubricant produced from these virgin oils, about 80 to 90% of production cost is due to virgin oil as a raw material. Thus researchers work on the cheap, easily available and ecofriendly options of WCO for the production of bio lubricants. Chowdhury *et al*. carried out a two-step process for conversion of WCO to bio lubricants [65], i.e. enzyme based hydrolysis followed by esterification with octanol. Hydrolysis catalysed by 1g per L of *Candida rugosa* lipase resulted in maximum 92% conversion when water to oil ratio was kept as 4 with free fatty acids as the end product after 30 h. Free fatty acids extracted with hexane then underwent the second step of esterification where Amberlyst 15H catalyst (2g) was used as catalyst. Octanol to FFA molar ratio of 3:1 with optimized temperature 80˚C was reported to give 98% conversion in 3 h.

2-3-3. Polyurethane products from WCO

Polyurethane products for coating and adhesive were also developed from WCO with two step process. Patented technology mentioned waste frying oil as a starting material that reacted with acids (e.g. performic acid) and produced epoxides. These epoxidised forms of WCO then generated polyols when reacted with alcohols. Reaction of polyol and isocynate then resulted in polyurethane products [66]. Biodegradability and other physical properties of polyurethane products obtained from WCO vary as per the type of cross linker or additive used [67], operating conditions used and composition of WCO. Biodegradable polyurethane sheet can be produced from WCO along with PEG and MDI as reactants. The polyurethane sheets obtained can also be incorporated with fibre glass and silica which generally offer change in properties like hardness [67].

2-3-4 Alkyd resin synthesis from WCO

Waste cooking oil without any pre-treatment can be used to produce commercially acceptable alkyd resins, which can further be used for coating applications in paints, inks, enamels, varnishes and lacquers [68]. In most reactions, for making alkyd resins, 10 to 65% by weight of WCO is used along with polycarboxylic acids and polyols. Formation of alkyd resin with such polycondensation reaction at high temperature (150˚C to 280˚C) generates water. For betterment of reaction, an excess amount of water needs to be removed by using distillation columns. According to inventor, produced resin has a broad range of molecular weight (500-6000 Mn). Researchers also found that, undesirable changes like Acrolein formation from glycerine may occur during the reaction. Such types of changes may cause deviation in desired properties of alkyd resins like color, molecular weight, viscosity. This can be avoided by carrying out reactions systematically [69].

2-4. Waste cooking oil as a component of animal feed

Oils and fats are essential components of animal diet as they serve high energy diets as well as some essential fatty acids are needed and are not synthesised by animals. This requirement is fulfilled in terms of vegetable oils which also bind the other ingredients of animal feed together [70]. Very economic source of these oils is WCO from deep fryers. Food provided to the animals like poultry farms and pigs, indirectly come to human beings via food chain. Thus components of animal food should be added consciously. It should be free from detergents, other liquids or solid material, scrapings from hot plates and other cooking utensils such as saucepans and fry pans, also the high concentration of some components like lipid peroxidises and other 2-thiobarbituric acid reactive substances. Initially WCO was filtered and directly used in the animal feed. Later on detailed studies of WCO based animal feed showed presence of some harmful components like dioxins [71]. This led to the establishment of some strict laws against the utilisation of WCO in animal feed. The European Commission has interpreted the use of used cooking oils from restaurants and catering facilities but not from the manufacturing premises until 2004. UK government allowed use of used cooking oil which is collected by a licenced waste carrier, treated well and certified to be used in animal feeds [72].

Composition of WCO is different from that of the vegetable oil due to thermal-reactions occurring during the frying. Increased amount of malondialdehyde and other 2-thiobarbituric acid reactive substances that were detected in WCO make it unfit as a component of animal feed. The maximum permitted level for TBARSs in animal and human consumption oils is 6 µg per g. Thus necessary purification steps should be taken before use of WCO in animal feed for the removal of lipid peroxidises and TBARSs. Conventional techniques like filtration, degumming, bleaching, and deodorizing processes failed in the removal of lipid peroxidises and TBARSs. Thus new methods were successfully tried by Zuojun Wei *et al.* [73]. Author used three methods, i.e., water extraction, physical adsorption, and chemical adsorption, where physical adsorption was done with four adsorbents, namely activated carbon, alumina oxide, activated clay, and HZSM-5 zeolite while chemical adsorption was done with three commercially available amino-containing materials, i.e., lysine, monosodium glutamate, and urea. Among all the methods Chemical adsorption is found to be the best and removed about 80% of both impurities in the presence of 0.1% H3PO4 [73]. Author mentioned chemical method as commercially applicable, effective and efficient method for WCO purification.

2-5. Waste cooking oil in soap formation

One of the easiest methods of utilising WCO is formation of soap or detergent which can be further used as dish washing, laundry washing, house cleaning, animal or vehicle cleaning or bath use, etc. Low grade soaps can be directly obtained by saponification method, i.e. reaction with alkali metal hydroxide (approximately 1-5 %) or sodium orthosilicate. These soaps can also be added to organic salt like citrate, glucanate, succinate and surface-active agents [74]. Use of such strong alkaline chemical compounds is not suitable due to its violent reactivity with carbon dioxide and humid air.

Another patented method of liquid soap or detergent formation from WCO is the use of amine derivatives such as alkanol amine, alkyl amine and alkylene amine and surface active agents such as salcosine salt, linear alkylbenzenesulfonate, alkylsulfonate, etc. This method is able to produce mild liquid soaps which are safe to handle. According to author, the given method is also able to eliminate peroxides from WCO, hence unpleasant odorous substances [75].

3. Conclusions

Waste cooking oil generated in huge quantities has miscellaneous applications as reviewed above. Although biodiesel production is one of the best possible applications of WCO all over the world, direct electricity generation systems like CHP and Steam engines are also efficient as reviewed above. These technologies are still in research and development stage and require an indepth study of process economics and process intensification for commercial applications. Secondary products like glycerol or value added products like biolubricants, greases, and polyurethane products also have great market potential. The same can be produced with minimum availability of WCO. Household generation of WCO can also be utilized in animal feed or soap formation for its waste management. Proper collection, transportation, purification and utilization of WCO make it a potential renewable source of energy rather than a form of waste. Dependence on vegetable oil for synthesis of products like biodegradable polymers, resins, greases will also be reduced by utilization of WCO with optimised processes. Extensive and serious research on utilization of WCO and potentially new applications will definitely solve the problems associated with WCO waste management in the modern world.

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