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Title: Progress in Waste Oil to Sustainable Energy, with Emphasis on Pyrolysis Techniques

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Abstract: This paper begins with a review on the current techniques used for the treatment and recovery of waste oil, which is then followed by an extensive review of the recent achievements in the sustainable development and utilization of pyrolysis techniques in energy recovery from waste oils. The advantages and limitations shown by the use of pyrolysis technique and other current techniques were discussed along with the future research that can be performed on the pyrolysis of waste oil. It was revealed that the current techniques (transesterification, hydrotreating, gasification, solvent extraction, and membrane technology) are yet to be sustainable or completely feasible for waste oil treatment and recovery. It was established that pyrolysis techniques offer a number of advantages over other existing techniques in recovering both the energetic and chemical value of waste oil by generating potentially useful pyrolysis products suitable for future reuse. In particular, microwave pyrolysis shows a distinct advantage in providing a rapid and energy-efficient heating compared to conventional pyrolysis techniques, and thus facilitating increased production rates. It was found that microwave pyrolysis of waste oil showed good performance with respect to product yield, reaction time, energy consumption, and product quality, and thus showing exceptional promise as a sustainable means for energy recovery from waste oils. Nevertheless, it was revealed that some important characteristics of the pyrolysis process have yet to be fully investigated. It was thus concluded that more studies are needed to extend existing understanding in the optimal reaction and process parameters in order to develop the pyrolysis technology to be a sustainable and commercially viable route for energy recovery from problematic waste oils.

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Date: 21 January 2015

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Submission of Review Manuscript to Renewable & Sustainable Energy Reviews

Please find enclosed our paper "**Progress in waste oil to sustainable energy, with emphasis on pyrolysis techniques**" for consideration for publication in your journal. All the work outlined in this paper is our own except where otherwise acknowledged and referenced. The work contained in the manuscript has not been previously published, in whole or in part, and is not under consideration by any other journal. All authors are aware of, and accept responsibility for, the manuscript.

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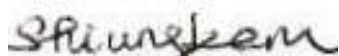
Rationale

The paper deals with the recent achievements in the use of various current techniques (i.e. membrane technology, solvent extraction, transesterification, hydrotreating, gasification) for the treatment and recovery of waste oil. This is then followed by an extensive review of the sustainable development and utilization of pyrolysis techniques in energy recovery from waste oils, a goal well-aligned with the motivation of this journal. The advantages and limitations shown by the use of pyrolysis technique and other current techniques was discussed along with the future research that can be performed on the pyrolysis of waste oil. This study extends existing understandings in energy recovery technology by demonstrating that pyrolysis offers a sustainable approach to the treatment and recovery of waste oils. The recovery of useful products for use as an energy source by pyrolysis technique shows many advantages over traditional destructive approaches and has demonstrated excellent potential for energy recovery from problematic waste oils. Thus we consider our work is of sufficient novelty and impact to appeal to the readership of the Renewable & Sustainable Energy Reviews; we hope you will agree.

Your consideration is much appreciated.

Thank you.

Yours sincerely



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**Progress in Waste Oil to Sustainable Energy, with Emphasis on Pyrolysis
Techniques**

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Abstract

This paper begins with a review on the current techniques used for the treatment and
recovery of waste oil, which is then followed by an extensive review of the recent
achievements in the sustainable development and utilization of pyrolysis techniques in

energy recovery from waste oils. The advantages and limitations shown by the use of pyrolysis technique and other current techniques were discussed along with the future research that can be performed on the pyrolysis of waste oil. It was revealed that the current techniques (transesterification, hydrotreating, gasification, solvent extraction, and membrane technology) are yet to be sustainable or completely feasible for waste oil treatment and recovery. It was established that pyrolysis techniques offer a number of advantages over other existing techniques in recovering both the energetic and chemical value of waste oil by generating potentially useful pyrolysis products suitable for future reuse. In particular, microwave pyrolysis shows a distinct advantage in providing a rapid and energy-efficient heating compared to conventional pyrolysis techniques, and thus facilitating increased production rates. It was found that microwave pyrolysis of waste oil showed good performance with respect to product yield, reaction time, energy consumption, and product quality, and thus showing exceptional promise as a sustainable means for energy recovery from waste oils. Nevertheless, it was revealed that some important characteristics of the pyrolysis process have yet to be fully investigated. It was thus concluded that more studies are needed to extend existing understanding in the optimal reaction and process parameters in order to develop the pyrolysis technology to be a sustainable and commercially viable route for energy recovery from problematic waste oils.

Keywords: Waste oil, used oil, sustainable energy, waste to energy, pyrolysis, microwave pyrolysis.

1. Introduction

Waste oils refer to contaminated or degraded liquid products that mainly consist of waste lubricating oil from machinery and cooking oil resulting from cooking operation. Waste lubricating oil is derived from engine oil, transmission oil, hydraulic, and cutting oils [1], whereas waste cooking oil is originated from cooking oil made from biological resources such as coconut, sunflower, soybean, palm tree, cottonseed, rapeseed, and olive.

Waste oils are well-known hazardous substances due to the presence of degraded additives and undesired substances that could bring about adverse impacts (e.g. carcinogenic, mutagenic, and reproductive effects) to human health and the environment (e.g. water and soil pollutions, frangible ecosystem, and climate changes). For cooking oil, its structure is altered by oxidation reaction via typical free radical mechanisms after an open air frying process. As a result, hydroperoxide is produced as a primary oxidation product and the hydroperoxide may further oxidize into very reactive and toxic products such as 4-hydroxy-2-alkenals [2], and thus making the waste cooking oil a hazardous waste [3]. The recycling of waste cooking oil as an animal feedstock is strictly prohibited in the European Union (EU) in order to prevent the carcinogenic components from transferring to the human body through food chain [4].

In 2010, the global consumption of lubricating oil was approximately 42 million tons and it is forecasted to hit 45 million tons by 2015 [5]. Due to the imperfection of machinery efficiency, about 50% of the lubricating oil ended up as waste lubricating oil after the operations and this resulted in the generation of 20 million tons of waste oil. Up to 30% of the generated waste oil was derived from Asia, whereas North America had contributed about 22% of the waste oil [5]. In addition, the EU has gobbled up 6 million

tons of lubricating oil in 2006 and in turn producing 3 million tons of waste lubricating oil to be disposed of [6]. On the other hand, waste cooking oil is also present as a problematic waste oil. The continual increase in human population will ensure a continuous food demand and consequently an inevitable generation of waste cooking oil. According to the estimation of global edible oil consumption from the U.S. Census Bureau, International Data Base, Internal Estimates (USDA), there are 145 million tons of edible oil being consumed in 2012 and it is expected to reach 660 million tons by 2050 from which palm oil ranks as the highest demand by the world population [7]. Steven (2003) [8] reported that catering and industrial sources in the UK have been synthesizing about 50,000 and 100,000 tons of waste vegetable oil annually, respectively. Moreover, there is an approximately 1 million ton of waste cooking oil being produced from French fries and snack food industries every year in the EU [9]. Thus, the increasing generation of waste oil in high volume has become a major concern for modern society.

The disposal of waste oil is a major challenge nowadays as the improper disposal of this hazardous waste could pose a direct hazard to the environment and human health. On account of the high management cost needed for the disposal of waste oil, illegal dumping of waste oil into the sewers and the sea could be the normal practice by irresponsible generators of waste oil and even by unsupervised government authorities. The discharge of waste oil into the ocean could endanger the marine life, especially the seabirds where the waste oil could adsorb on their feathers and in turn disable their delicate hooks and barbs that are usually functioned as a protection of their skin from long-term exposure to water, thus making the seabirds vulnerable to cold water and eventually causing their death from hypothermia [10]. Additionally, the hydrophobic

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4 nature of waste oil could create a layer of oil on the surface of the water that could inhibit
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6 the oxygen dissolution and leading to an increase of the chemical oxygen demand (COD)
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8 levels in the water [9]. Recently, the dumping of waste cooking oil into the sewers has
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10 created a serious problem that has become a public concern in China and Taiwan. It was
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12 revealed that some greedy and heartless companies are making huge profits by converting
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14 the waste hogwash oil collected from the sewers into cooking oil using only simple
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16 treatment procedures; the waste hogwash oil refers to the waste oil disposed from the
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18 processing and frying of waste animal parts and organs [11]. The 'badly-refined' cooking
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20 oil, containing undesirable substances such as polycyclic aromatic hydrocarbons (PAHs)
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22 and heavy metals (e.g. nickel and lead), is then released to the market and sold to
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24 restaurants at a cheap price, and in turn poisons the customers who have eaten the food
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26 cooked with the 'badly-refined' cooking oil in those restaurants [12]. Another common
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28 disposal of waste oils is by incineration. Incineration results in the release of greenhouse
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30 gases (e.g. CO₂) that contributes to climate changes. Moreover, this method also leads to
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32 toxic emission of flue gas containing PAHs, fly ash, and dangerous polychlorinated
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34 compound [13].
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44 Owing to the problematic nature of waste oils that could cause a series of negative
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46 chain reactions to human health and the environment, the development of an
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48 environmentally safe, sustainable, socially acceptable, and cost-effective solution should
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50 be taken as a primary consideration for the treatment, recovery, and disposal of waste oil
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52 [14]. There are some techniques that have been exploited in order to tackle the problems
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54 derived from the disposal of waste oil and to formulate the feasibility and sustainability
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56 of waste to energy conversion [15]. Waste to energy is an energy recovery application
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that employs waste processing technologies to produce energy or valuable materials from waste materials (e.g. biomass, plastics, waste oils, and sewage sludge). This review presents and discusses the current methods used for the treatment and recovery of waste oil. Then, emphasis is focused on the sustainable development and utilization of pyrolysis techniques in waste oil recovery. The advantages and limitations shown by the use of pyrolysis technique and other current techniques are presented and discussed along with the future research directions.

2. Current Methods for Waste Oil Treatment and Recovery

The global energy crisis has attracted countless of researchers to direct their interest towards the research on waste to energy province in order to formulate good solutions for sustainable and renewable energy supply. There have been various researches conducted on the conversion of waste oil to energy by multifarious technologies in the past 10 years. Some of the applications are presented and discussed in the following sections.

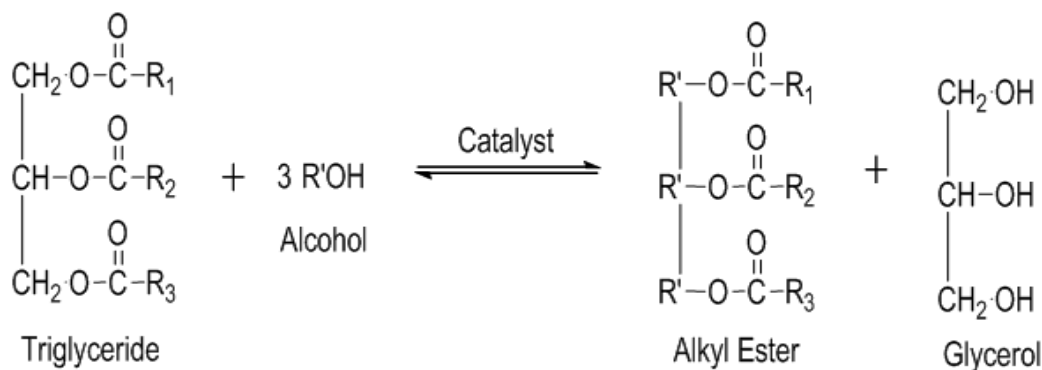
2.1 Transesterification

Transesterification (also known as alcoholysis) is a chemical process to transform an ester compound into another ester compound by means of interchanging or substituting the alkyl moiety (R'/R'') from alcohol source. This process can be catalyzed by acids (e.g. H₂SO₄, HCl), bases (e.g. NaOH, KOH), or enzymes (e.g. lipase) [16]. The utilization of the different types of catalyst in the transesterification process is determined by the free fatty acid (FFA) content (0.5 to 15 wt%) in waste cooking oil [17]. For waste cooking oil with a high FFA content (>1 wt%), acid-catalyzed transesterification is more effective

than base-catalyzed transesterification [18], while the base-catalyzed reaction is used when the FFA content is less than 1 wt% [20]. The FFA is a long chain hydrocarbon bonded to a carboxylic acid moiety (e.g. oleic acid). According to Kulkarni & Dalai [3] and Shuli et al. [21], the base catalyst that is utilized in the transesterification process could react with the FFA present in the waste cooking oil and this will lead to soap formation. Consequently, the base catalyst is deactivated by the FFA and thus decreasing the desirable product yield (e.g. alkyl ester). In contrast, acid catalyst will not contribute to the soap formation and it could achieve up to 90% conversion of waste cooking oil to alkyl ester products in acid-catalyzed transesterification [19]. However, the base-catalyzed reaction is a more preferable option for commercial applications as compared to acid-catalyzed reaction because the acid-catalyzed reaction requires a longer reaction time, which can go on up to 10 hours or even 69 hours as reported by Wang et al. [19] and Freedman et al. [22], respectively. On the other hand, enzyme-catalyzed transesterification offers an advantage over both the acid and base-catalyzed reactions in which the FFA content in the waste cooking oil has negligible effect on the enzyme-catalyzed transesterification. Unfortunately, the operational cost of the enzyme-catalyzed reaction is very expensive in larger scale operation due to the high cost of the enzyme [23].

Transesterification process has been commercialized at industrial level in biodiesel production in which the reaction happens in between an alcohol (usually methanol) and triglycerides (originated from waste vegetable oil and animal fat) that results in the production of alkyl ester compound as biodiesel and glycerol as a by-product. **Eq. (1)** depicts the general chemical pathway for transesterification process. The resulting ester

compound possesses similar fuel properties (e.g. density, cetane number, and heating value) compared to commercial diesel fuel and thus making the alkyl ester compound suitable to be used as a biodiesel [24].



Eq. (1)

At present, studies on transesterification have been extended towards the application of synthesized catalysts as reported in the literatures, e.g. transesterification of waste cooking oil by alumina-supported MnZr catalyst [25] and alumina-supported CsZr catalyst [26]. These studies showed that the reaction with alumina-supported catalyst demonstrated better yield of fatty acid methyl ester (FAME) product (up to 93%) compared to the reaction without the use of catalyst. The authors also reported on the optimum reaction conditions (catalyst loading, methanol to waste oil ratio, reaction time, reaction temperature) to obtain the maximum yield of FAME. A comparison of the optimum reaction conditions needed for alumina-supported catalysts (i.e. MnZr and CsZr) is shown in **Table 1**. Additionally, Hindryawati & Maniam [27] have refined this method by combining transesterification with the use of ultrasound technology and waste marine sponge as a catalyst to treat waste cooking oil. The authors found that a remarkable yield (up to 98 wt%) of methyl ester was obtained in only an hour of reaction time at 55°C. They also found that the waste marine sponge could resist soap formation by not reacting

with the FFA (up to 6%) in the waste cooking oil. The authors have concluded that their work should be prioritized for biodiesel production in the future.

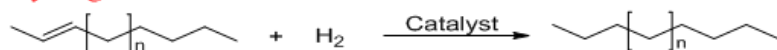
Although transesterification has been commercialized and the method is practically proven, this method still possesses some disadvantages such as the need for a large quantity of alcohol by means of reaction stoichiometry since 1 mole of triglyceride is reacted with 3 moles of alcohol as shown in **Eq. (1)**, and the final product could show lower oxidation stability due to the presence of oxygen that could lead to poor storage [28].

2.2 Hydrotreating

Hydrotreating is an established industrial refinery process employed in the production of transportation fuels from petroleum. Hydrotreating employs a high volume of hydrogen gas to remove the undesired impurities (e.g. sulphur, nitrogen, and oxygen) from the petrochemical feedstock in order to reduce the emission of environmental pollutants (e.g. SO_x and NO_x) during fuel consumption, and also to boost up the cetane number of the fuel products (e.g. diesel and gasoline) in order to produce higher quality fuels. Recently, there have been studies performed on hydrodeoxygenation of waste oil [29, 30] with the aim of synthesizing oxygen-free biodiesel and to overcome the low oxidation stability of the products obtained from the transesterification process of waste oils, e.g. hydrodeoxygenation treatment of waste cooking oil over nanocatalyst by Zhang et al. [31], and hydrodeoxygenation of waste fat over a Pt/alumina catalyst by Madsen et al. [32]. However, high operation cost could be needed for this method due to the need to use a huge amount of hydrogen gas. Moreover, hydrogen volume is even more demanding when hydrodenitrogenation process is involved based on stoichiometric

calculations from which 2 moles of hydrogen is needed to remove 1 mole of nitrogen in order to generate NH₃ gas as a by-product. **Eq. (2-5)** shows the common hydrotreating process used in removing the undesired impurities (e.g. sulphur, nitrogen, and oxygen) present in the petrochemical feedstock.

Hydrogenation



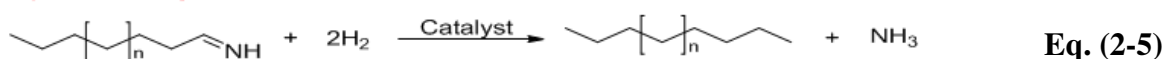
Hydrodesulfurization



Hydrodeoxygenation



Hydrodenitrogenation



2.3 Gasification

Gasification is a partial oxidation process that is used to generate useful gaseous products (e.g. CO, CO₂, H₂, and CH₄) from carbon-containing materials such as coal, biomass, waste oils, and natural gas. The syngas (H₂ and CO) obtained from this method could act as a precursor to the production of diesel-like fuel via Fischer-Tropsch synthesis pathway. Gasification is deemed to be a promising technology for waste oil recovery as reported by Guo et al. [33]. Their results showed a remarkable hydrogen yield from co-gasification of waste engine oil with bio-oil (an oil product derived from pyrolysis of corn-straw). Gasification has also been widely applied in electricity generation and some internal combustion engines. This technology is likely to be an ideal and practical method for waste to energy application if the extremely high process temperature (up to 1600°C) [34], which is the main limitation of this technology, can be reduced to a lower process temperature.

2.4 Solvent Extraction

Solvent extraction is a separation technique that utilizes an organic solvent to separate the components of a mixture. The solubility of the solvent and the components and their polarity nature (e.g. polar or non-polar) are the key factors behind this method. The unwanted aromatic components present in waste oils can be selectively separated out by suitable organic solvent and the remaining saturated components could eventually enhance the oxidative stability of the treated oils [35]. In addition to the use of conventional solvent extraction to treat waste oils, there have been research conducted on treating waste lubricating oils by combining solvent extraction with other techniques, such as thermal degradation in strong base aqueous solution followed by solvent extraction [36], and combination of solvent extraction and adsorption on solids [37]. It was revealed that these method offer advantages in providing high oxidation stability of the recovered oil and the separated compounds could be highly selective. Despite the flexibility of this method, there are some drawbacks that could have caused the method to become unfavorable to waste oil recovery. Firstly, the extraction requires the use of a high volume of solvents, and secondly the construction of the extraction plants could be costly due to the need for a high pressure sealing system, and thirdly the types of solvent used could be hazardous (e.g. benzene) or flammable (e.g. propane) in nature.

2.5 Membrane Technology

This technique employs various types of polymer hollow fiber membranes to treat waste oils by filtration in order to remove the carbon soot and metal particles present in the waste oil and to regain some lubricating properties of the oil. The most common types of polymer that have been used as the membrane filter are polyethersulphone (PES),

polyvinylidene fluoride (PVDF), and polyacrylonitrile (PAN). Tur et al. [38] have performed surface modification through the use of hexamethyldisiloxane (HMDSO) on PES membrane. The PES membrane is then treated using radio frequency plasma to improve the hydrophobicity of the membrane surface before the PES membrane was used as a filter for waste frying oil. Their result showed that polar compounds and free fatty acid contents have been selectively filtered by the modified PES membrane. The treated frying oil showed lower viscosity and could be re-used as frying oil. Although this method showed advantages in providing a low process temperature (40°C) and pressure (0.1 MPa), the membranes are costly and could easily be damaged by large particles [39]. In addition, it is thought that this technique only removes the polar compounds and free fatty acid contents of the waste oil, however, it is not clear whether the possible presence of other undesirable species (e.g., PAHs) is detected and removed by this technique.

3. Pyrolysis for Conversion of Waste Oils to Energy

For almost a century, waste oils have been treated and reused as a temporary fuel during and after the war [40, 41]. There was a serious shortage of fuel after World War II in 1947 and as a result significant amounts of tung oil (also known as chinese wood oil) were utilized as the feedstock to produce motor fuels in order to overcome the shortage [42]. It was found that the tung oil consists mainly of fatty acid chain with C₁₈ carbon chain (i.e. 9Z,11E,13E- α -elaeostearic acid) [43], and thus the oil was used as a feedstock for biodiesel production in 1947 due to this chemical content.

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4 It was also revealed that the existing technologies for waste oil treatment and
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6 recovery (See Section 2.1 - 2.5) are yet to be both technical and economical feasible in
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8 addition to complying with the concept of being a sustainable and eco-friendly approach.
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10 Thus, an alternative technology should be developed in order to effectively treat and
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12 recycle waste oils by transforming the oils into value-added materials. Pyrolysis
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14 technique has recently shown to be a potential alternative to convert waste oils into
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16 potentially useful fuel products and chemical feedstock, though the use of this technology
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18 is not widespread as yet.
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23 24 *3.1 Pyrolysis* 25 26

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28 Pyrolysis is a thermal process that heats and decomposes a substance at high
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30 temperature (300-1000°C) in an inert environment from which oxygen is excluded. The
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32 thermal process has nowadays been utilized to convert waste materials into useful
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34 pyrolysis products. There has not been a consensus on which is the main pyrolytic
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36 product since various observations were reported by researchers and these could be
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38 accounted by factors derived from the waste composition and experimental conditions
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40 (e.g. reaction temperature, vapor residence time, and heating rates) [44]. In general,
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42 pyrolysis produces three classes of products, namely: solid char residues, waxy liquid oil
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44 compounds, and incondensable gases. The process can be optimized to maximize
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46 production of any of these constituents by altering parameters such as process
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48 temperature and reactant residence time [45] e.g. a high temperature and high residence
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50 time promotes the production of gases; a high temperature and low residence time
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52 (termed “flash pyrolysis”) results in increased yield of condensable liquid oil products,
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54 and a low temperature and heating rate leads to increased char production [46] or to no
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4 chemical reactions taking place at all. The wide variety of pyrolysis products indicates
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6 that the products may need to be separated and purified before they can be used further;
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8 this can usually be achieved through the use of existing distillery and refinery facilities.
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12 Pyrolysis can be used as a feedstock recycling technique for hydrocarbon wastes,
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14 where the waste materials are cracked to produce hydrocarbon oils, gases, and char. This
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16 process is particularly useful in treating wastes of high hydrocarbon content (containing a
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18 mixture of long hydrocarbon chains) whereby the long hydrocarbon chain ($>C_{50}$) can be
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20 thermally broken down into shorter hydrocarbon chain (C_1-C_{12}) that could be used as a
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22 petrochemical or chemical feedstock. Although pyrolysis process for waste oil treatment
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24 has not been fully exploited, this process has been receiving considerable attentions from
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26 researchers nowadays on its potential to produce energy-dense products from waste
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28 materials [47]. Recently, there were findings on the pyrolysis transformation of sewage
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30 sludge into tar-free fuel gas [31] and polyaromatic hydrocarbons [48]. There were also
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32 pyrolysis studies on plastic wastes, catechol, acetylene and ethylene, and co-pyrolysis of
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34 the scrap tires with waste lubricating oil by other researchers [49-52].
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42 For the past two decades, research on pyrolysis processes has been conducted using
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44 several types of equipment heated by conventional heating source (e.g. an electrical gas
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46 heater), namely: melting vessels, blast furnaces, tubular or fixed bed reactors [53]; these
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48 types of pyrolysis processes are termed generally as ‘conventional pyrolysis’. These types
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50 of equipment were used in a manner where the thermal energy is externally applied to the
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52 reactor and heats all the substances in the reactor including the evolved pyrolysis-
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54 volatiles, the surrounding gases, and the reactor chamber itself. In this case, energy is not
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56 fully targeted to the material being heated and this results in significant energy losses in
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terms of the energy efficiency of the whole process. Nevertheless, several of these processes have been developed into a pilot plant scale despite their limited energy efficiency [54]. Pyrolysis has been performed using electrical furnace as the heating source as shown by Ben Hassen-Trabelsi et al. [55] and Jimenez-Cordero et al. [56].

3.2 Conventional Pyrolysis of Waste Oil

Pyrolysis techniques have been developed as an alternative to treat and recycle waste oil, though the use of this technology is not widespread as yet. Most literature reports focus on pyrolysis using conventional electric resistance heating [52, 57-65]. Studies on waste oil using conventional pyrolysis have been conducted by University of Alicante, University of Zaragoza and Institute of Carboquimica in Spain, Ankara University, Ege University, Dicle University, Dokuz Eylul University, Sila Science, University of Batman, University of Gaziantep, and University of Mahalleli in Turkey, in addition to Korea University, Korea Institute of Energy Research, and Dong Hae University in South Korea. The institutions in Spain and Turkey use cylindrical, tubular and fluidized bed reactors heated by either electric furnace, oven, or heater [52, 57-61, 63, 64, 66], whereas the Korean institutions employ stirred batch reactors heated by either jacketed electric heater [62], autoclave, or molten salt bath [67, 68]. Most of these pyrolysis studies have been performed using waste oil on its own [57, 63-66], while some have been performed in the presence of coal [69-71], scrap tyres [52], or zeolite and alumina catalysts [59].

Song et al. [72] has recently examined the use of electric arc heating to pyrolyse the waste oil. The electric arc pyrolysis of waste oil employs a different heating mode compared to conventional electric-heated pyrolysis. An electric arc cell or generator was used to generate momentary electric discharge for pyrolyzing the waste oil in order to

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4 produce high-value fuel gases (e.g. hydrogen and acetylene) and ‘usable’ carbonaceous
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6 residue. It is considered as a flash pyrolysis process whereby the waste oil is rapidly
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8 heated to 1300-1500°C for 0.01-1 s, producing incondensable gases and carbonaceous
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10 residues as the pyrolysis products. Although this technique shows potential as a disposal
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12 method for waste oil, such technique should be investigated further due to concerns over
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14 the presence of undesirable species (e.g. PAHs, metals, and mixed oil-additive polluted
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16 residues) in the pyrolysis products [73].
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22 In the past decades, there have also been researches on the use of conventional
23
24 pyrolysis process for recovery of waste oil of a biomass nature (i.e. waste cooking oil,
25
26 waste vegetable oil) [74-77]. It has been reported that the waste oils contained long-chain,
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28 saturated, and unbranched hydrocarbons and they showed a nearly similar hydrocarbon
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30 contents to diesel fuels [78]. Consequently, vigorous efforts have been made to produce
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32 fuel products from the pyrolysis of different types of waste vegetable oil, e.g. the
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34 pyrolysis conversion of sunflower oil into bio-fuels such as bio-diesel and bio-gasoline
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36 [79, 80].
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42 *3.2.1 Kinetic Study*

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45 Briefly, numerous kinetic models have been proposed by previous authors for the
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47 conventional pyrolysis of waste oil and so far there has not been a consensus on which is
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49 the dominant model. In addition, the existing literature is limited to pyrolysis performed
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51 in batch or semi-batch operation in which the waste oil was added initially into a batch
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53 system before being subjected to pyrolysis. A standard, power-law kinetic model has
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55 been most frequently proposed as the kinetic model, as it represents very well the overall
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57 pyrolysis process [60, 61]. Nevertheless, some authors have proposed a different model
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4 for the pyrolytic reaction, where the kinetic model is composed of more complex
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6 equations. For instance, Kim and Kim [67] proposed a lumped model for the pyrolysis
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8 mechanism of waste oil that assumes the formation of pyrolytic products occurs by a
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10 combination of series and parallel reactions. The disagreement above indicates that
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12 further study is needed to improve the understanding of waste oil pyrolysis kinetics.
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15 There have been no reports on the kinetic model describing microwave or electric arc
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17 pyrolysis of waste oil. It is thought that the kinetic model describing the microwave or
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19 electric arc pyrolysis will be related to the models proposed by previous authors for
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21 conventional pyrolysis.
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25 26 27 *3.2.2 Pyrolysis Products* 28 29

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31 Pyrolysis techniques have recently shown promise as an environmentally friendly
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33 disposal method for waste oil [65, 72, 81] – the waste material is thermally cracked and
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35 decomposed in an inert atmosphere producing hydrocarbon oils, gases, and char. The
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37 main advantage of pyrolysis is that it has the potential to recover both the energy and
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39 chemical value of the waste oil by generating potentially valuable products from the
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41 pyrolysis process. The oil and gaseous products demonstrated a high calorific value, and
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43 the char produced can be used as a substitute for carbon black. In particular, the gaseous
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45 product is of considerable interest due to its potential as a source of hydrogen fuel. Other
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47 advantages compared with steam reformation processes include negligible production of
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49 toxic oxidized species (e.g. dioxins, NO_x) [82, 83], less energy consumption and the
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51 production of a disposable solid waste (char) [81]. Due to its ability to produce
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53 potentially valuable products, vigorous efforts have been made to perfect the pyrolysis
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55 process and techniques for the recycling of waste oil in addition to offering an alternative
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4 solution to the disposal of the waste by incineration. In view of that, the aim of the
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pyrolysis process would be to obtain valuable products that can be further used in other
chemical processes and should demonstrate a commercial opportunity rather than a
problem for the disposal of waste oil. Thus, research on pyrolysis processes of waste oil
has always concentrated effort on clarifying the variation of product spectra with the type
of pyrolytic equipment, the nature of the load, and the process conditions.

So far there has not been a consensus on what are the main products during the
pyrolysis of waste oils. In fact, there have been many explanations for the differences
observed in the experiments conducted by different researchers, although some
researchers have managed to obtain somewhat similar product yields. In general, three
classes of product are obtained from the pyrolysis, that is: gases, oils, and char. **Table 2**
shows an example of the different yields of products obtained by different sets of
researchers investigating waste oil pyrolysis.

In contrast to the results presented in Table 2, high yields of solid residues (20 wt%)
were observed in some conventional electric-heated pyrolysis processes [57]. The
residues are likely to be a mixture of residual unpyrolyzed waste oil and char. It is
thought that the high yields of solid residue can be accounted for by incomplete
decomposition that occurred during the pyrolysis, which was performed at a low
temperature for quite a long period; the waste oil was heated to 330°C and maintained for
1 hour before being subsequently heated to 600°C. The residues are a sludge-like mixture
of oil and solid additives [84, 85]. It is envisaged that the solid residue would need further
treatment in order to improve the viability of such pyrolysis approach. High yields of oil
product (85–92 wt%) were also reported in several conventional electric-heated pyrolysis

processes [52, 58, 62]. It is thought that a significant portion of the oil product is derived from distillation or evaporation that occurs during the heating of waste oil. These processes transfer hydrocarbons from both the uncracked and 'less-cracked' fractions of waste oil in the reactor to the condensation system and thus into the recovered oil product. Evaporation has also been observed in several pyrolysis studies of waste oil [60, 61].

In addition to the differences in product yield, varied product spectra were also found in the different studies. Moliner et al. [66] obtained high yields of valuable alkanes, light olefins, and light aromatics of BTX (benzene, toluene, xylene) in their waste oil pyrolysis study. Next, Lázaro et al. [69] reported even higher proportions of methane and light olefins (ethylene and propylene) though with a comparatively lower production of BTX in the pyrolysis products. The similarities and differences in these studies were postulated to be mainly due to the influence of operating or experimental conditions (i.e. temperature and pressure).

Later, in contrast with the previous studies, Nerín et al. [64] reported a similar yield of light olefins in the gaseous fraction but very high yields of aromatics of up to 67% of the oil fraction. The aromatics in this fraction include the methyl derivatives of benzene and naphthalene in addition to BTX. These authors conducted pyrolysis studies with different industrial waste oils (hydraulic, machine, automotive, and cutting oil), and produced conclusions on the influence of the composition of waste oil on the pyrolysis product, e.g. a high content of $<C_{24}$ hydrocarbons in the waste oils results in increased yield of gaseous products, and a high content of $>C_{24}$ hydrocarbons leads to increased yield of aromatic compounds in the oil product. In addition, several compounds were

found in the gaseous product, namely: H₂, CO, CO₂, and H₂S, together with minor amounts of other light hydrocarbons [63].

However, toxic metals were surprisingly found to be present in the oil fractions following condensation of the pyrolysis products from waste oil [64]. According to the authors, metals (e.g. Pb, Fe, Cu, and Ni) are mainly present in the oils as metallic compounds; these compounds would turn into volatiles during the pyrolysis process at a reaction temperature of 600°C and above. In addition, some metals (e.g. V, Cd) are condensed (accumulated) on the particulate matter produced during the process [86]. As a result, the metals condensed on the particulate matter and the metallic compounds (depending on their volatility) are likely to escape from the pyrolysis chamber with the other gaseous products during the pyrolysis process, causing the formation of undesired oil products containing toxic metals. As a result, efforts are being made to incorporate additional processes such as hot gas cleaning and previous demetalisation of waste oils in order to obtain oil products that are free of metals.

Toxic semi-volatile PAH compounds such as naphthalene, phenanthrene, anthracene, fluoranthene, pyrene and the highly carcinogenic benzo(a)pyrene were also detected in the gaseous product by Fuentes et al. [60] in their waste oil pyrolysis study. Thus, these studies imply that further investigation is needed to perfect the pyrolysis process conditions in order to improve the production of valuable pyrolysis products whilst controlling the formation of potentially toxic compounds described above.

It was established that current pyrolysis techniques (mostly conventional electric-heated pyrolysis processes), when compared to incineration and steam reformation processes, offers a number of advantages and shows excellent potential for treating the

waste oil. However, such practices possess limitations and there are still problems that exist at present associated with these pyrolysis techniques. The low thermal conductivity of engine oil (0.15-0.30W/m.K) often necessitates a long process time due to the low rate of heat transfer within the oil in order for pyrolysis to occur. Furthermore, in conventional electric-heated pyrolysis, the waste oil is heated by an external heating source which also heats all the substances in the heating chamber including the evolved pyrolysis-volatiles and the chamber itself. This results in significant energy losses and can also promote undesired secondary reactions of the evolved pyrolysis-volatiles that lead to formation of toxic compounds (e.g. PAHs) [87-89] and increased production of char [81], which can cause problems such as coking on the reactor wall and fouling of the system with particulates. In addition, the oil product generated from conventional electric-heated pyrolysis of waste oil was found to contain significant amounts of heavy PAHs (≥ 4 rings) with high risks of toxicity [87, 90]; hence, the resulting product cannot be directly used and consequently needs to be treated by an additional process for future re-use. Moreover, the uneven distribution of heat produced in some conventional pyrolysis processes has led to poor control over the heating process; as a result, the final fractions obtained from the pyrolysis are often varied and critically depend on the actual process conditions applied to the waste oil [63]. It was also found that the existing literature is limited to pyrolysis performed in batch or semi-batch operation in which the waste oil was added initially to a batch system before being subjected to pyrolysis. Limited information is therefore available concerning the characteristics of the pyrolysis of waste oil (e.g. the influence of key process parameters on the product distribution) when the pyrolysis is performed in a continuous operation. Owing to the limitations, inconsistent performance, and uncertainties shown by conventional pyrolysis, it is

important to improve the existing pyrolysis techniques or find an alternative pyrolysis technique to rectify these deficiencies in order to ensure better performance and control of the pyrolysis process as well as the production of more desirable pyrolysis products.

3.3 Microwave Pyrolysis

Microwave pyrolysis is a thermo-chemical process that has recently been applied in waste to energy application. The main difference between microwave pyrolysis and conventional pyrolysis is the use of a different heating source to generate the pyrolysis process, and in turn shows a different mode of heat transfer from the heating source to the target materials. In conventional pyrolysis, heat is directly converted from electrical energy which then reaches the surface of target material through conduction and convection, then the heat energy is transferred from the surface to the inner part of the target material; as a result, the heating is limited by the temperature of that surface in addition to the physical properties of the materials being heated such as the density and heat capacity of the material. On the contrary, microwave pyrolysis shows a different way of heating where the heating effect arises from the interaction of electromagnetic wave with the dipoles within the material being heated. By such heating effect, heat is generated within the target material rather than from an external source, thereby giving a more efficient heating process compared to conventional surface heating with respect to even distribution of heat and easier control over the heating. In addition, high temperatures and heating rates can be obtained through microwave heating [91], and it shows remarkably high conversion efficiency of electrical energy into heat (80%-85%) [92]. A simple comparison between the heat transfer in conventional and microwave pyrolysis is illustrated in **Figure 1**.

On the other hand, there were studies performed on microwave pyrolysis that employs a different approach by using microwave radiation as an indirect heat source to heat and pyrolyse waste materials [13]. In this approach, waste material is pyrolysed by contact with a bed of microwave absorbent heated by microwave radiation (e.g. particulate carbon). The highly microwave-absorbent absorbs enough microwave energy and heats up initially to achieve the desired temperature for the pyrolysis cracking and subsequently pyrolyse the waste material to produce a variety of different products. This type of microwave pyrolysis process, which involved the pre-heating of microwave absorbent followed by the transfer of heat to the waste material in order for cracking to occur, may present a different heating mechanism and produced a different outcome compared to that reported in conventional pyrolysis of waste materials.

3.3.1 Historical Background of Microwave, from Military Purpose to Food Processing

The origin of microwave power can be traced back in 1940 where it is generated from a very high-power generator called the magnetron. According to Stuerger [93], a magnetron that can generate a high power output (about 100 kW on a pulse basis) was initially developed at the University of Birmingham by Randall and Booth. Later on, research has moved towards the use of microwave magnetron in navigation and communications equipment for military purpose before and during World War II. In 1945, scientists have proved that microwave power can be used to generate heating and this in turn led to the invention of the first microwave oven prototype by P. L. Spencer from Raytheon Company in 1952. Further investigation of microwave heating on food had been performed at the Department of Food Technology of Massachusetts Institute of Technology, and this resulted in the development of microwave food processing

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4 technology in commercial scale in 1960. In between 1970s and 1980s, there was mass
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6 production of domestic oven, which has led to the production of microwave oven after
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8 years and years of modification and improvement.
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10 11 12 *3.3.2 Principles of Microwave Heating* 13 14

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16 Microwave is an electromagnetic wave that locates in between the infrared (IR) and
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18 the radio wave regions of the electromagnetic spectrum. The frequencies of microwave,
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20 range from 300 MHz to 300 GHz, which correspond to a wavelength ranging from 0.001
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22 m to 1 m. Despite the broad range of frequency available for microwave, there are only
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24 two frequencies applicable to microwave heating as permitted by Federal
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26 Communications Commission (FCC), which are 915 MHz and 2.45 GHz with the aim of
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28 preventing interferences with telecommunication devices and equipment [94-96].
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34 Microwave comprises of two components that are perpendicular to each other,
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36 namely the electric and magnetic field as shown in **Figure 2**. There are four types of
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38 materials that interact differently with microwave irradiation: i) The insulator or
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40 microwave-transparent material, ii) the conductor, iii) the absorber, and iv) the mixed
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42 absorber [97]. The insulator refers to material that enables microwave to penetrate
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44 through without incurring any losses of the microwave. In contrast, microwave tends to
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46 bounce back and cannot pass through the conductor. The absorber (also known as
47
48 'dielectrics') is able to fully absorb microwave radiation and heat up, hence the resulting
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50 of microwave heating which is also known as dielectric heating. The mixed absorber is a
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52 composite or multi-phase material that consists of a phase of high dielectric loss material
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54 and another phase of low dielectric loss material [97]. Mixed absorber shows advantage
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56 in providing selective heating whereby the microwaves could be absorbed by the high
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dielectrics loss material and in turn generate heat for heating the low dielectrics loss material [97]. Hence, the low dielectrics loss material present in mixed absorber could undergo a better heating effect compared to the low dielectric loss material that is directly exposed to the microwave. The interaction between microwave irradiation and the material being heated is governed by the dielectric loss tangent of the material ($\tan \delta$) as defined in **Eq. 6** below:

$$\tan \delta = \text{dielectric loss factor, } \epsilon'' / \text{dielectric constant, } \epsilon' \quad \text{Eq. 6}$$

The $\tan \delta$ is a very useful ratio in examining the efficiency of a microwave heating process, particularly the heating rate and the final temperature that can be achieved by microwave-heated material [98] as these two parameters are strongly dependent on the dielectric loss factor and the dielectric constant of the material. The dielectric loss factor determines the efficiency of conversion from microwave energy to heat energy, whereas the dielectric constant determines the amount of microwave energy being absorbed and reflected by the material. Material that possesses a $\tan \delta$ value lower than that of distilled water (~ 0.1) is categorized as microwave-transparent (e.g. wood), whereas material with a higher $\tan \delta$ value (> 0.1) than that of distilled water is classified as microwave-absorber that shows good dielectric properties. Typical microwave-absorbers that show a high capacity to absorb and convert microwave energy into heat are carbon materials (e.g. particulate carbon, activated carbon) and inorganic oxides [99]; the $\tan \delta$ of carbonaceous materials has been reported by Mushtaq et al. [100]. Thus, microwave-absorber is of interest to researchers nowadays since it can easily be heated up by microwave radiation and in turn acts as a reaction medium in the microwave pyrolysis process. The microwave pyrolysis process is closely related to three heating mechanism by which materials are

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4 heated in a microwave field, namely, dipole polarization, interfacial or Maxwell-Wagner
5 polarization, and conduction mechanism [13, 100], whereas the complete principles and
6 theories behind microwave heating are well understood and available in several textbooks
7 [95, 101].
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10 11 12 13 14 15 *3.3.3 Microwave Pyrolysis of Waste Oil* 16

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18 Microwave pyrolysis has recently been developed as an alternative to convert waste
19 oil into potentially useful products [102-105]. The microwave pyrolysis system (**Figure 3**)
20 was operated with an electrical power input of 7.5 kW and was capable of processing
21 waste oil at a flow rate of 5 kg/h with a positive energy ratio of 8 (energy content of
22 hydrocarbon products / electrical energy supplied for microwave heating) and a net
23 energy output of 179,390 kJ/h [105]. By pyrolysing the waste oil in a modified microwave
24 oven in the presence of a bed of particulate-carbon as the microwave-absorbent, light
25 hydrocarbons and H₂ are generated and these have potential for use as either an energy
26 source or industrial feedstock [102, 105]. The authors claimed that the use of a bed of
27 particulate-carbon as the heating medium is important to achieve the high temperature in
28 order for the extensive pyrolysis of waste oil to occur. The waste oil was found to possess
29 poor dielectric properties due to its non-polar nature [106], therefore it requires heating
30 by contact with materials with high microwave absorbency in order to achieve pyrolytic
31 thermal cracking [105].
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53 The pyrolysis products were found to consist of useful gaseous products containing
54 light C₂-C₆ hydrocarbons with light olefins, light aliphatics, and syngas (CO, H₂) that
55 could potentially be used as a gaseous fuel and chemical feedstock [102]. The hydrogen
56 obtained can be potentially used as a second-generation fuel, and the CO could be steam-
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4 reformed to produce more hydrogen, whereas the light hydrocarbons can be extracted for
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6 use as chemical feedstock. The gaseous product could be burned directly in gas engine or
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8 upgraded to produce hydrogen as a clean fuel.
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12 The pyrolysis also produced a considerable yield (88 wt%) of a liquid oil product
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14 containing potentially valuable light aliphatic and aromatic hydrocarbons (e.g. benzene,
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16 toluene, xylene (BTX), and benzene derivatives) [103]. The oil product was found to
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18 possess fuel properties comparable to commercial gasoline fuel [105], and it is also
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20 relatively contaminant free with a low content of sulphur, oxygen, and residue, and is
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22 almost entirely free of metals [104]. Additionally, the authors claimed that the oil product
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24 show a low toxic risk and contain negligible or minor amounts of toxic polycyclic
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26 aromatic hydrocarbons (PAHs) compounds [104]. The oil product could be added to
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28 petroleum refinery as a chemical feedstock for further processing to produce useful
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30 industrial chemicals and products, or it could potentially be upgraded to transport grade
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32 fuels, although further studies are needed to confirm these possibilities. **Figure 4** shows
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34 that the oil product obtained from microwave pyrolysis of the waste oil was a fairly pale-
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36 yellowish-gold liquid oil.
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45 Additionally, the microwave pyrolysis was found to produce a char product that
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47 contained the majority of metals originally present in the waste oil, providing a
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49 convenient opportunity for the efficient recovery of these metals [104]. The char can be
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51 readily separated from the particulate-carbon particles by sieving, and the particulate-
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53 carbon bed can be repeatedly re-used as the microwave-absorbent (heating medium) after
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55 the separation, as a result of the fact that the majority of the metals were found to be present
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4 within the char particulates, resulting in very low levels of residual metals being retained
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6 within the particulate-carbon bed itself.
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10 The product compositions were found different to those formed in conventional
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12 pyrolysis of waste oils. The authors claimed that this could be attributed to the unique
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14 heating mode and the chemical environment present during microwave pyrolysis. It has
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16 been reported that process temperature played a significant role in the yield and formation
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18 of different types of products. Lam et al. [103, 106] demonstrated that the highest
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20 conversion of waste oil into liquid oil product was obtained at a pyrolysis temperature of
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22 550°C with considerable yield of valuable compounds in the oil product. Moreover, the
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24 authors found that microwave pyrolysis was able to reduce remarkable content of metal
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26 contaminants, sulfur, and oxygen originally present in the waste oil.
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33 Studies have also been reported on the microwave pyrolysis of vegetable oil for the
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35 production of biofuel [107]. The authors have performed microwave pyrolysis
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37 experiments on rapeseed oil. A 2 kW microwave oven with a frequency of 2.45 GHz was
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39 employed as the heating source and it was connected to a manual three-stub-tuner (IBF
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41 Electronics). In this study, a simulated waste vegetable oil (SWO) was tested instead of
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43 real-world waste vegetable oils because the authors claimed that the uncontrolled thermal
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45 cycles and cooking conditions could give rise to significant variation between the batches
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47 of oils collected. It was concluded by the authors that the liquid products contained small
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49 amounts of light hydrocarbons but large amount of aromatic compounds. It was found
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51 that the addition of catalyst could improve both the yield of aromatic compound and the
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53 conversion of vegetable oil (i.e. rapeseed oil) into biofuel.
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Overall, the authors demonstrated that microwave pyrolysis offers an exciting new approach to convert problematic waste oils into potentially useful products that could be used as a fuel or a chemical feedstock. Thus, microwave pyrolysis of waste oil is a potentially desirable process that deserves further attention with regard to its potential for treating and recycling waste oil. However, it was revealed that there are still little understandings of its application to waste oil treatment and recovery and knowledge of the pyrolytic behaviour of waste oil is still poor and there are still gaps to be filled in order to fully exploit the advantages of this process. Therefore, more work is needed to develop a technical feasible microwave pyrolysis process to handle the increased production of waste oil.

3.4 Comparison of Pyrolysis with Other Current Techniques in Energy Recovery from Waste Oil

There have been many efforts on the application and research of various techniques to treat and convert waste oil into an energy source. **Table 3** summarizes the advantages and limitations shown by pyrolysis and other current techniques in energy recovery from waste oil. It was revealed that there are several limitations shown by with the current techniques (membrane technology, solvent extraction, transesterification, hydrotreating, gasification). These limitations could be attributed to the high operation cost, the need to use large amounts of reagents and solvents (e.g. H₂ gas, benzene, membrane, alcohol), and the undesired yield and composition of the resulting products. It was thus concluded that the current techniques are yet to be fully feasible for waste oil treatment and recovery.

On the other hand, it was established that conventional pyrolysis techniques show advantages in providing a system that is simple and inexpensive to build and it generates

oil products for use as a potential fuel, but it has some limitations with respect to the slow heat transfer and the resulting long reaction time. In particular, microwave pyrolysis show a distinct advantage in providing a rapid and energy-efficient heating compared to conventional pyrolysis techniques, and thus facilitating increased production rates. However, it was revealed that microwave pyrolysis still possesses limitations and there are still problems that exist at present associated with this pyrolysis technique. It was found that limitation information is available concerning the technical information for designing commercial equipment for the pyrolysis of waste oil, e.g. the optimal design of the pyrolysis reactor, the microwave cavity, and the microwave magnetron. Moreover, some important characteristics of the pyrolysis process have yet to be fully investigated such as the optimization of key process parameters (e.g. microwave power, heating rate, the need of catalyst, the use of different materials as the microwave absorbent) on the yield and chemical composition of the product. Thus, the growth of industrial microwave pyrolysis applications could be hampered by an apparent lack of the understanding of the pyrolysis systems and also the high cost of microwave magnetron.

4. Future Directions

It was revealed that pyrolysis shows great potential as a promising technology for waste oil recovery. This technology not only provides a route to recover potentially useful products from environmentally hazardous waste oils, but it also serves as an effective disposal method for the waste oils. Thus, it would be worthwhile to carry on researching further aspects of the pyrolysis of waste oil in order to explore the full

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4 potential of this process. Thus, the studies proposed below are some of the routes that
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6 could be explored as future work in the pyrolysis of waste oil.
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10 An improved microwave pyrolysis system can be developed by studies on the use of
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12 different types of microwave ovens. The type of microwave oven (e.g. single-mode
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14 versus multimode) is deemed to have an influence on the yield and composition of the
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16 pyrolysis products. Dominguez et al. [113] have reported that single-mode microwave
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18 oven could enhance gas production while the multimode microwave oven could lead to
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20 increased char production from the microwave pyrolysis of sewage sludge. In addition,
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22 the authors claimed that the multimode microwave oven could improve the dehydration
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24 and cracking processes that occurred during the pyrolysis process.
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30 Catalytic pyrolysis has shown advantages over non-catalytic reaction [114-116]. It
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32 has been reported that zeolites, metal oxides, inorganic additives, and microwave
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34 receptors (e.g. graphite, active carbon, glass fibre) can be used as a catalyst to improve
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36 the product selectivity in pyrolysis process [117-119], e.g. increasing the recovery of oil
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38 or gaseous product from the pyrolysis process. According to Maher & Bressler [40], there
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40 are several types of catalysts that have been tested in the conversion of vegetable oils into
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42 biofuel products (e.g. bio-gasoline and bio-diesel), such as molecular sieve catalysts,
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44 activated alumina catalyst, transition metal catalyst, and sodium carbonate. Thus, it is
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46 envisaged that different catalysts could be studied and utilized in the pyrolysis of waste
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48 oils in order to develop a catalytic pyrolysis system suitable for waste oil recovery. On
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50 the other hand, the dielectric and heating characteristics of these materials should be
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52 examined in order to assess their potential to be used as the microwave-absorbent to heat
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54 and pyrolyse waste oil in the microwave pyrolysis process. Some of these materials (e.g.
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4 metal oxides) are highly microwave-absorbent and they have been reported to show a
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6 high conversion efficiency of microwave energy to thermal energy when heated by
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8 microwave radiation [99, 120], and thus the use of these materials could improve the
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10 absorbance of microwave energy and increase the amount of energy that can be recovered
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12 from the system.
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17 An economic analysis is an important factor that determines the viability of a
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19 recycling process, especially in the scale-up of the operation for commercial applications.
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21 It must be acknowledged that the market penetration for pyrolysis application is still low
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23 despite the many advantages shown by this technology. This could be attributed to the
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25 reluctance to replace old technology (e.g. the current applications for waste oil recovery)
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27 with new yet unfamiliar technology, the lack of knowledge of the fundamentals of
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29 pyrolysis technology, and the lack of incentive and encouragement by governmental
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31 authorities (e.g. tax reduction or exemption) to use and develop this technology. Thus, it
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33 would be desirable to present an economic assessment of the pyrolysis technique used in
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35 energy recovery from waste oil. It is envisaged that future work could be performed to
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37 produce an economic assessment of the feasibility of scaling up the pyrolysis operation
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39 for commercial applications.
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48 It is thus envisaged that future work could be performed to investigate the influence
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50 of other process parameters on the yield and composition of the pyrolysis products, such
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52 as residence time, microwave power, carrier gas flow rate, and a mass ratio between
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54 absorbent and sample. In particular, a thermogravimetric analysis or kinetic study of the
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56 pyrolysis decomposition of waste oil could be performed to determine the kinetic
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58 parameters required to propose a kinetic model for the pyrolysis process (e.g. the
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apparent activation energy, order of reaction, and apparent pre-exponential factor that can be calculated from the degree and rate of weight conversion). The kinetic model will be useful for determination of the optimal process conditions to maximise the yields of valuable compounds in the pyrolysis products, and for the design and simulation of the pyrolysis process for commercial applications. Pyrolysis process can also be performed on mixture of waste oil that consists of waste cooking oil and waste lubricating oil. A study conducted by Singhabhandhu & Tezuka [41], has demonstrated that a combination treatment could offer advantage on cost saving from waste collection and management. Thus, it is envisaged that future work could be performed by co-pyrolysis of waste oils.

5. Conclusion

Despite the variety of research that has been conducted on the use of pyrolysis technology for waste oil treatments and recovery, this technology is still a relatively new process compared to other existing technologies, and there are limited informations available on the pyrolysis of waste oil such as the optimal reaction parameters and the suitable design of pyrolysis system. Thus, the growth of industrial pyrolysis applications is hampered by an apparent lack of the understanding of the pyrolysis systems and the technical information for designing commercial equipment for the pyrolysis of waste oil. Consequently, the use of pyrolysis technology for waste oil recovery has not been extensively exploited despite the many advantages shown by pyrolysis. It was revealed that some important characteristics of the pyrolysis process have yet to be fully investigated such as the optimization of key process parameters on the yield and chemical composition of the product and the effects of the use of catalyst. Thus, more studies are

needed to obtain these information in order to develop the technology to be both technical and economic feasibility for energy recovery from waste oil.

So far, there has been little research reported on the pyrolysis of waste oil, and existing literature is limited to mostly studies performed nearly one decade ago on conventional electric-heated pyrolysis of waste oil. It was established that current pyrolysis techniques offer a number of advantages and show excellent potential for treating the waste oil. However, it was found that such practice possesses limitations and uncertainties and there are still gaps to be filled in order to fully exploit the advantages of using pyrolysis process to treat the waste oil.

On the other hand, the economics of pyrolysis of waste oil is greatly dependent on the quality and yield of the pyrolysis products. It was revealed that a very wide spectrum of pyrolysis products ranging from methane to aromatic compounds can be expected the pyrolysis of waste oil. Nevertheless, the characterization of the products obtained during pyrolysis of different types of waste oil is still an important aspect to study; as has been stated in previous sections, several authors claim to have obtained different product yields and spectra in different waste oil pyrolysis processes. Thus, it is expected that the product spectra obtained in pyrolysis of different types of waste oil could be different to those found in previous pyrolysis studies of waste oil due to the different natures of the waste oils being treated.

In summary, this review has revealed several aspects of pyrolysis of waste oil that need to be examined to investigate whether pyrolysis technique is optimized for conversion of waste oil into products for use as an energy source. In view of the ability of pyrolysis techniques to treat and transform waste oils into potentially useful hydrocarbon

products, it would be worthwhile to carry on researching further aspects of pyrolysis of waste oils in order to explore the full potential of this process. The optimization of this process and the subsequent scale-up to a commercial scale will depend on how well the parameters involved in this new process and their relationship are understood.

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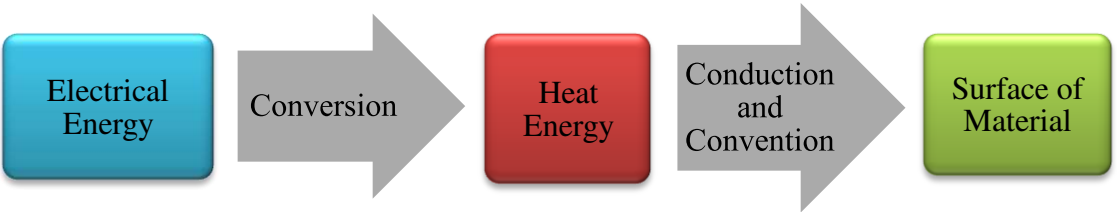
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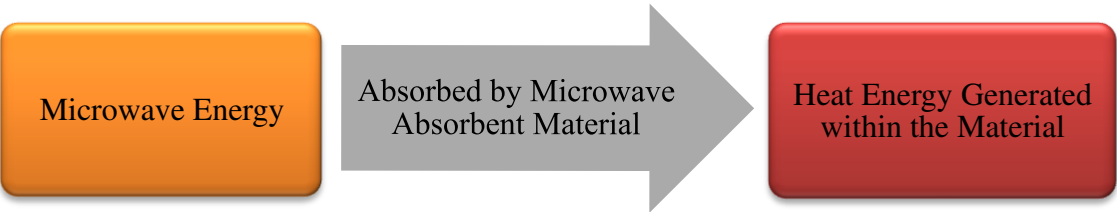
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1 For Conventional Pyrolysis:



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3 For Microwave Pyrolysis:

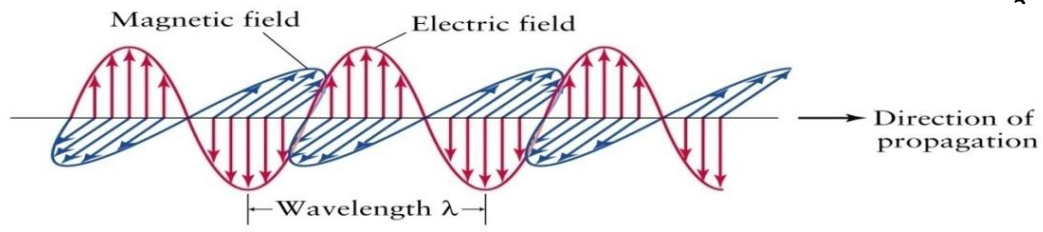


4

5 **Figure 1.** Heat transfer in conventional pyrolysis and microwave pyrolysis

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Figure 2. The magnetic and electric field components in microwave.

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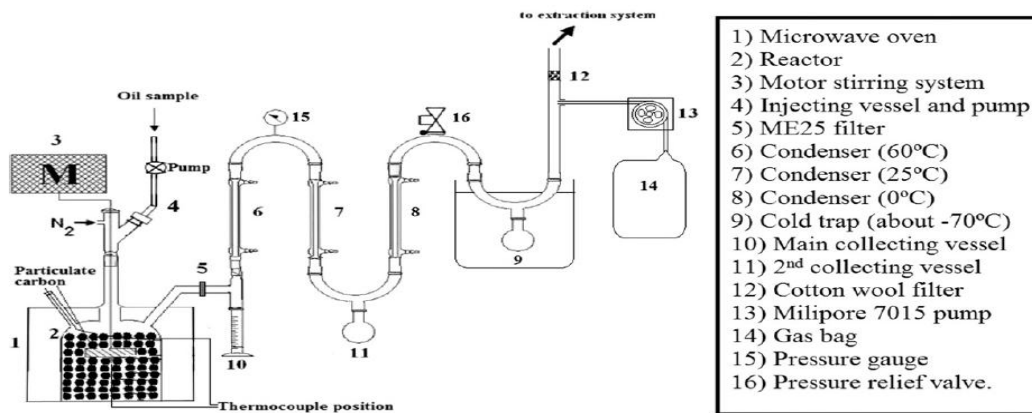
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Figure 3. Schematic layout of microwave pyrolysis system [106]

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Waste oil

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Pyrolysis oil

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Figure 4. Liquid oil product from microwave pyrolysis of waste oil [106]

8

1 **Table 1**

2 Comparison of the optimum reaction conditions for alumina-supported MnZr catalyst and
3 alumina-supported CsZr catalyst for maximum yield of FAME.

Catalyst	Alumina-supported MnZr [25]	Alumina-supported CsZr [26]
Catalyst Loading	2.5 %	3.0 %
Reaction Temperature	150°C	65°C
Reaction Time	5 Hours	3 Hours
Methanol to Waste Oil Ratio	14:1	30:1

4

5

1 **Table 2**

2 Product yield (wt%) of waste oil pyrolysis processes.

Research	Gases	Oil	Char
Moliner et al. [66]	34.6	60.4	5.0
Nerín et al. [64]	50.4	46.2	3.4
Lázaro et al. [70]	44.7	50.6	4.7
Gómez-Rico et al. [61]	52.1	N.R.	N.R.
Uçar et al. [52]	10.0	88.4	1.6
Fuentes et al. [60]	1.2	N.R.	N.R.
N.R. - Not Reported			

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1 **Table 3**

2 Advantages and limitation shown by pyrolysis and other existing technologies in energy
3 recovery from waste oil.

Technology	Advantages	Disadvantages
Membrane Technology	<ul style="list-style-type: none"> • Low process temperature (40°C) and pressure (0.1 MPa). • Improve liquidity and flash point of the recovered oil. 	<ul style="list-style-type: none"> • The membrane used could be expensive and easily damaged, and fouled by large particles [39].
Solvent Extraction	<ul style="list-style-type: none"> • Selective separation of target compounds. • Enhance oxidation stability of recovered oil [35]. 	<ul style="list-style-type: none"> • High investment cost. • The use of hazardous (e.g. benzene) or flammable solvent (e.g. propane).
Transesterification	<ul style="list-style-type: none"> • Selectively production of desired fatty acid. • The by-product (glycerol) can be transformed into ethanol [108], polyglycerol [109], and act as fuel additives [110, 111]. 	<ul style="list-style-type: none"> • High process cost due to the use of large volume of alcohol (3 moles alcohol to 1 mole triglyceride) • Final product possesses low oxidation stability and leads to a short storage period.
Hydrotreating	<ul style="list-style-type: none"> • High product recovery. • High oxidation stability of product [29, 30]. 	<ul style="list-style-type: none"> • High operation cost due to the need for large volume of hydrogen gas.
Gasification	<ul style="list-style-type: none"> • High yield of hydrogen gas. 	<ul style="list-style-type: none"> • High process temperature (1600°C).
Conventional Pyrolysis	<ul style="list-style-type: none"> • High feedstock flexibility. • Simple system and inexpensive to construct [112]. • Production of potential gasoline range oil products [79, 80]. 	<ul style="list-style-type: none"> • The need for high process temperature (usually up to 1000°C). • Slow heat transfer leads to longer reaction time. • Production of PAHs compounds as by-product [87].
Microwave Pyrolysis	<ul style="list-style-type: none"> • Fast and selective heating lead to shorter reaction time. • Less PAHs compounds produced. • More environmental 	<ul style="list-style-type: none"> • Not all materials used are conducive to microwave absorption. • Reactor design, microwave cavity, microwave

friendly with less magnetron yet to be
greenhouse gases emission. optimized.

- Products possessed many potential uses.
 - Possibly high cost of the whole system set-up.
 - Limited information available on key process parameters (e.g. microwave power, heating rate, catalyst, microwave absorbent).
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