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A Review on Pyrolysis of Protein Rich Microalgae Biomass

Krishnakumar P[1], Dr. S Suresh[2], Dr. Prashant Baredar[3]
[1,3]Energy Centre, [2]Chemical Engineering dept, MANIT, Bhopal

Abstract —The population explosion and rapid urbanization currently being experienced in both the developed and developing economies of the world calls for enormous quantities of fuel and this high rate of fuel consumption is heavily dependent upon conventional non-renewable energy resources. It is well known that these conventional resources would be extinguished in the near future and moreover cause a lot of problems related to pollution, climatic changes, etc. To tackle this precarious energy deficit scenario and to reduce the negative environmental impacts, alternative fuels from renewable energy sources are gaining more and more attention. Biofuel, an alternate renewable fuel, is derived usually from biodegradable feedstock like vegetable oils, animal fats, etc. However, various kinds of protein based waste products can also be utilized for the production of biofuels, which has an added advantage of minimizing waste and reducing environmental pollution. Proteins are large macromolecules consisting of one or more long chain amino acids. This review paper focuses on cost effective technologies and processes particularly focusing on the utilization of protein rich biomass and pyrolysis to convert biomass into useful liquid biofuels and by-products. Pyrolysis is a process in which the waste materials are burned in the absence of oxygen or air at elevated temperatures which results in the thermal cracking of long chain protein molecules into smaller sub chains. A few studies suggests that pyrolysis of protein-rich microalgae can also produce bio-oil that, in some respects, is superior to bio-oil from lignocellulosic biomass. It was also reported that bio-oil from microalgae was characterized by lower oxygen content and a higher heating value than bio-oil from lignocellulosic biomass. Studies conducted by Miao et al. reported bio-oil yields of 18%, 24% and 57.9% for pyrolysis of Chlorella protothecoides, Microcystis aeruginosa and heterotrophic C. protothecoides, respectively. In this review paper an analytical study on the pyrolysis of high protein content biomass is performed on the basis of a number of studies.
Keywords: Pyrolysis, Proteins, Microalgae, bio-oil, Chlorella vulgaris

I. INTRODUCTION

The population explosion and rapid urbanisation currently being experienced in both the developed and developing economies of the world calls for enormous quantities of fuel and this high rate of fuel consumption is heavily dependent upon conventional non-renewable energy resources. It is well known that these conventional resources would be extinguished in the near future and moreover cause a lot of problems related to pollution, climatic changes, etc. To tackle this precarious energy deficit scenario and to reduce the negative environmental impacts, alternative fuels from renewable energy sources are gaining more and more attention. Biofuel, an alternate renewable fuel, is derived usually from biodegradable feedstock like vegetable oils, animal fats, etc. However, various kinds of protein based waste products can also be utilised for the production of biofuels, which has an added advantage of minimising waste and reducing environmental pollution. Proteins are large macromolecules consisting of one or more long chain amino acids. This long chain amino acids can be broken down into smaller one's by thermal cracking in the absence of oxygen. Usually, thermal cracking of protein rich biomass occurs at 500-800^{o}C. The main products of pyrolysis of protein feedstokes are in solid, liquid and gaseous forms. In solid form, the product of pyrolysis is commonly known as bio-char and in liquid form, it is known as bio-oil. The bio-oils produced from the pyrolysis of biomass is usually a dark brown liquid. It is composed of complex structures of alcohols, acids, aldehydes, ketones, esters, sugars, phenols, pyrrole, nitriles, amides, and other aromatics and aliphatic hydrocarbons. Bio-oil contains the significant potential to be used as a source of energy. In addition, various useful chemicals can be extracted from bio-oil obtained from the pyrolysis of protein-based compounds.

II. PYROLYSIS

Pyrolysis is a thermal cracking process in which the materials are thermally heated in the absence of oxygen or air to reduce the percentage of carbon dioxide in the product. Pyrolysis has the potential for converting protein-rich biomass into bio-oil which can be further upgraded to fuels and chemicals of more applicable form [1]. Fast Pyrolysis yields three type products. In the gaseous state, the product is a flammable mixture of carbon monoxide, hydrogen, carbon dioxide, and light hydrocarbons suitable for generating process heat [1]. The solid bio-char product is primarily composed of long chain aromatic hydrocarbon and contains mineral components present in the feedstoke [1, 2]. Bio-char can be used in various potential applications. It is commonly used as a soil amendment and as carbon sequestration agent [2]. The liquid bio-oil product from pyrolysis is a high viscosity, dark-brown liquid. It is composed of numerous organic and inorganic components along with up to 15–20 wt% water. Bio-oil can be upgraded potentially to fuels through hydro-processing and catalytic cracking [1,2]. Compared to the pyrolysis of lignocellulosic biomass with low-protein content, relatively little is known about the pyrolysis of biomass with high protein and lipid content. Pyrolysis is done in a reactor consisting of closed chamber able to withstand high temperatures. The reactor used for pyrolysis can be classified in numerous ways but basically, it is classified into two, based on the movement of materials through the reactors. Accordingly, reactors are classified into fixed and fluidized bed reactors. Fixed bed reactors are primarily used for the production of charcoal by carbonisation process. Usually, this process yields liquid products. It is called fixed bed reactor because the feed remains same in the reactor bed. In this process, usually the feed is fed into the reactor and heat is applied externally. Nitrogen is generally used as inert atmosphere which helps the gaseous product to dispose of in the reactor. The losses in the fixed bed reactors are less compared to fluidized bed reactor [17]. Fluidized bed reactors utilise vessels containing heated particles, such as catalyst particles or inert sand. The bed is fluidized by passing inert gas or recycled product gas through the bed. Biomass residues are injected into or above the hot bed by a solid feeder, such as screw feeder or intermittent solid slug feeder [18]. Kaige Wang et al., Hansson et al. and Weimin et al all used fluidizes bed reactors for their experimental works.Wood et al. [3,4] examined pyrolysis of corn DDGS to produce bio-oil and bio-char as a potential opportunity for expanding markets for DDGS and improving the sustainability of the corn ethanol industry. Their study showed that the yields of bio-oil produced from DDGS were comparable to those produced from lignocellulosic biomass [3,4]. The gas chromatography/mass spectrometry (GC/MS) analysis indicated that the bio-oil from microwave pyrolysis of DDGS contained a series of aliphatic and aromatic hydrocarbons [36]. Boateng's [6,7] group pyrolyzed barley-derived DDGS, pennycress press cake, and other protein-rich biomass in a fluidized bed reactor. Relatively higher yields of bio-oil with high-energy density were obtained from DDGS, compared with those obtained from lignocellulosic biomass. Boateng's group also found that bio-oil from high protein biomass exhibited better thermal stability than that from low-protein biomass [7]. Few studies performed [8,9] suggests that pyrolysis of protein-rich microalgae can also produce bio-oil that, in some respects, is superior to bio-oil from lignocellulosic biomass. Miao et al. [9] characterised the bio-oil from microalgae containing lower oxygen content and a higher heating value compared to the bio-oil obtained from lignocellulosic biomass. Miao et al. reported that he achieved bio-oil yields of 18% and 24% from the pyrolysis of Chlorella protothecoides and Microcystis aeruginosa, respectively. Another study by this group showed that by controlling the growth conditions of microalgal could impact the yield and composition of the resulting bio-oil [10]. They also reported that 57.9% yield of bio-oil was obtained from the fast pyrolysis of heterotrophic C. protothecoides. Grierson et al. [10] compared performance of pyrolysis of six different species of microalgae's in a tubular reactor. It was performed in slow heating conditions. Observations and calculations from the experiments indicated that the process was self-sustaining. In spite of numerous advantages of pyrolysis of protein based microalgae, bio-oil from those protein-rich biomass contains a high content of nitrogen. This may poison catalysts during bio-oil up-gradation and produce unaccepted nitrogen oxides during combustion [1, 3, 5, 11, 12]. Therefore, methods to remove nitrogen must be devised if transportation fuels are the final products from DDGS. The major disadvantage of pyrolysis of algal biomass that was reported by different researchers is the presence of high nitrogen content, which then appears in the bio-oil product. Most of this nitrogen exists as protein in fast-growing autotrophic microalgae [13]. Other main nitrogenous constituents present in microalgae are chlorophyll, nucleic acids, glucose amides and cell wall materials. The nitrogen content in microalgae due to compounds other than protein is less than 0.6 wt.% and due to protein compounds it is 10 wt.% [13]. By comparison, in lignocellulosic crops, the amount of nitrogen present is generally less than 1wt.%.

III. MATERIAL AND METHOD

This review paper concentrates mainly on pyrolysis of protein rich biomasses. Main protein rich biomasses are microalgal remnants, protein rich vegetables and naturally occurring protein fibres. Here we concentrate mainly on the pyrolysis of protein rich microalgal remnants. Microalgal biomass consists of lipids and proteins from which lipids are first extracted by solvent extraction process or by converting it into biofuel. The remnants of the microalgal are rich sources of protein. Kaige Wang et al. investigated the recovery of nutrients and energy from microalgal remnants by pyrolysis. Chlorella vulgaris (C.vulgaris) biomass was initially solvent-extracted to recover the lipid content then the remnants were used for the pyrolysis experiments. Pyrolysis was done using a fluidized bed reactor at a temperature of 500^{o}C [14]. A strain of Chlorella vulgaris (C.vulgaris) was cultivated in a 3800L closed indoor tubular photobioreactor. C.vulgaris was grown at room temperature with continuous illumination (338 μmolm-2s-1) and

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constant removal of both CO_2 and air. Flow rates of air and CO_2 were 25 and 3 L/min, respectively. The spectrophotometer of UV with a wavelength of 550nm was used to monitor the algae growth [14]. The algae were then harvested with the help of in-line continuous solid bowl centrifuge. The dewatered remnant biomass is then stored at room temperature after drying. Hansson et al. used shea nut meal (i.e. the residue after oil extraction is referred as shea), bark pellets, soya beans, yellow peas and whey protein as protein rich feedstock and pyrolyzed these in a fluidized bed reactor between 700 and 1000 °C one at a time. The whey protein powder was first compressed and then made into a disk-like forms. Fragments were then cut out from disk-shaped compressed whey protein. The fragments weighted between 115 to 175 mg [15] and they were as thin as 1 mm. The soya beans samples weighed 145 to 250 mg and they were approximately 3–5 mm thick. The yellow peas were 250–280 mg, 4–6 mm thick [15]. Bark pellets were cut into small pieces of bark weighing 200–260 mg and with 4- mm sides. Larger pieces of shea were cut into small fragments of size 3–5 mm weighing 250–260 mg. Pyrolysis of bark, whey and soya beans were done at 700, 800, 900, and 1000 °C. Pyrolysis of shea and yellow peas were done at 900 °C [15].

Two autotrophic microalgae's Chlorella protothecoides (CP) and spirulina platensis (SP) were pyrolysed up to 800^{o}C at heating rates of 15, 40, 60 and 80^{o}C/min in a TG analyser by Weimin et al [16]. Strains of CP and SP were obtained and cultivated in the suitable environment. CP and SP are grown with continuous illumination at 23 and 28^{o}C, respectively. Centrifugation was adopted to harvest the algal cells and the harvested cells are then washed with distilled water and then dried at 30°C under infrared light [16]. Small samples were prepared by pulverising in mortar in order to eliminate the heat transfer during the pyrolysis process and finally stored in desiccators.

IV. RESULTS AND DISCUSSIONS

A. Feedskoke Characterization

In this paper, the main protein rich biomass considered as feedstock is microalgal remnants. Pyrolysis of different types of protein rich microalgae has been studied and investigated by different researchers have been summarised in this paper. In general, protein, lipid and carbohydrate are the main components of microalgae, while cellulose, hemicellulose and lignin are the three main components of lignocellulosic biomass. Protein contents were 41.51and 61.24wt.% for C.vulgaris and C.vulgaris remnants, respectively. The total lipid content of C.vulgaris was only 15.67wt.%, although the amount is strongly dependent upon the algae species and growth conditions [19]. Due to the partial extraction of lipids from algal by the methods explained in the study, 5.71wt.% lipid still remained in the remnants. Proximate analysis and biochemical compositions of different microalgal biomass and the micro-algal remnants are given in Table I.

Table I
Proximate and biochemical compositions and higher heating values (HHV) of fast pyrolysis feedstocks [20]

Feedstoke	Proximate analysis (wt.%)				Biochemical composition (wt.%)			
	Moisture	Volatile	Fixed Carbon	Ash	HHV (MJ/kg)	Lipids	Proteins	Carbohydrates
C.vulgaris	6.18	66.56	11.52	15.67	16.8	15.67	41.51	20.99
C.vulgaris remnant	4.39	72.68	14.59	8.34	19.4	5.71	61.24	20.34

Results obtained from the ultimate and trace elemental analyses of C.vulgaris and C.vulgaris remnants are given in Table 2. From table II it is clear that C.vulgaris and C.vulgaris remnants had similar carbon and hydrogen contents compared to lignocellulosic biomass while the nitrogen content of the microalgal biomass was much higher than lignocellulosic biomass. The mineral contents present in algal biomass were several times higher than those found in lignocellulosic biomass. This high content of inorganic minerals in microalgae has a significant effect on the pyrolysis product distribution as has been demonstrated for carbohydrate pyrolysis [21].

Table II

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Elemental and inorganic content of fast pyrolysis feedstocks (dry basis) [20]

Feedstoke	Elemental analysis (wt.%)				Elemental analysis (mg/kg)				
	C	H	N	O	P	K	Na	Mg	Ca
C.vulgaris	42.51	6.77	6.64	27.95	32500	11140	593	13460	19960
C.vulgaris remnant	45.04	6.88	9.79	29.42	15520	8416	118	3670	1766

B. Pyrolysis Product Yields and Distribution

Bio-oil, bio-char and gas yields for pyrolysis of C.vulgaris remnant in a fluidized bed reactor is shown in Fig.1.Data for pine pyrolysis in a fluidized bed reactor at 520oC is also given for comparison [20]. The total bio-oil yield from C.vulgaris remnants was 53wt.%.

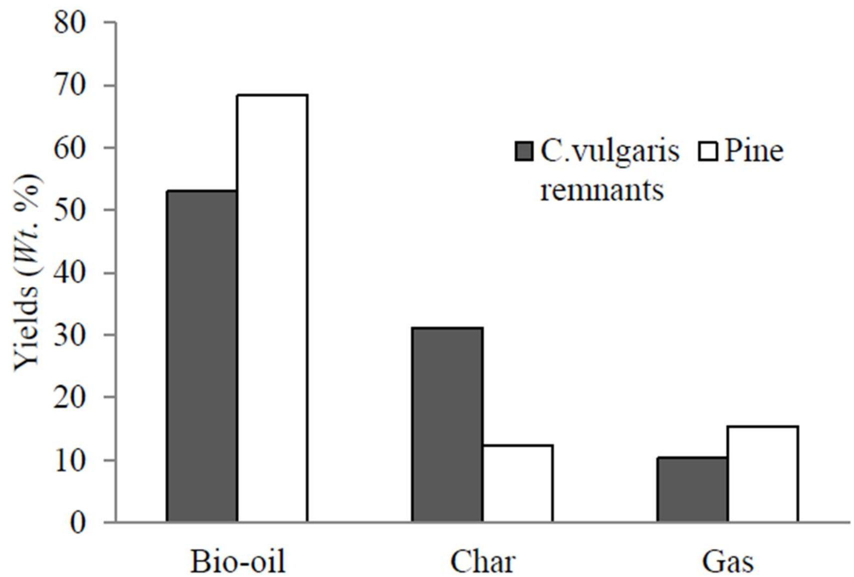

Fig 1. Comparison of fast pyrolysis product yields for C.vulgaris remnants (this study)and pine wood [20]

The bio-char yield was 30wt.%, which is much higher than the bio-char yield observed for the fast pyrolysis of lignocellulosic biomass which is usually 10-15 wt.%. This increase in bio-char yield may be partially due to the higher ash content in the algal remnants. The gas yield was 10wt.%, which is comparable to the gas yield for lignocellulosic biomass. The overall mass balance for the experiment was 94wt.%.

V. CONCLUSIONS

Pyrolysis of microalgal remnants using a fluidized bed reactor demonstrates a huge potential to recover energy and nutrients from protein rich biomass after lipid extraction. In this study, the performance of pyrolysis of C.vulgaris and its remnants has been analysed. It was observed that the bio-oil yield is around 53wt.% for protein rich biomass and the product mainly contains aromatics, amides, amines, carboxylic acids, phenols and fatty acids. The high nitrogen content of the bio-oil (12.8 wt.%) was attributable to the high protein content of the protein rich feedstoke. The biochar yield from the fast pyrolysis of C.vulgaris remnants is 30wt.% . Around 94% of the energy content of C.vulgaris remnant can be recovered as bio-oil and biochar products. From this study, it is evident that the pyrolysis can be effectively utilised to convert the energy content present in the microalgae remnants into more useable form.

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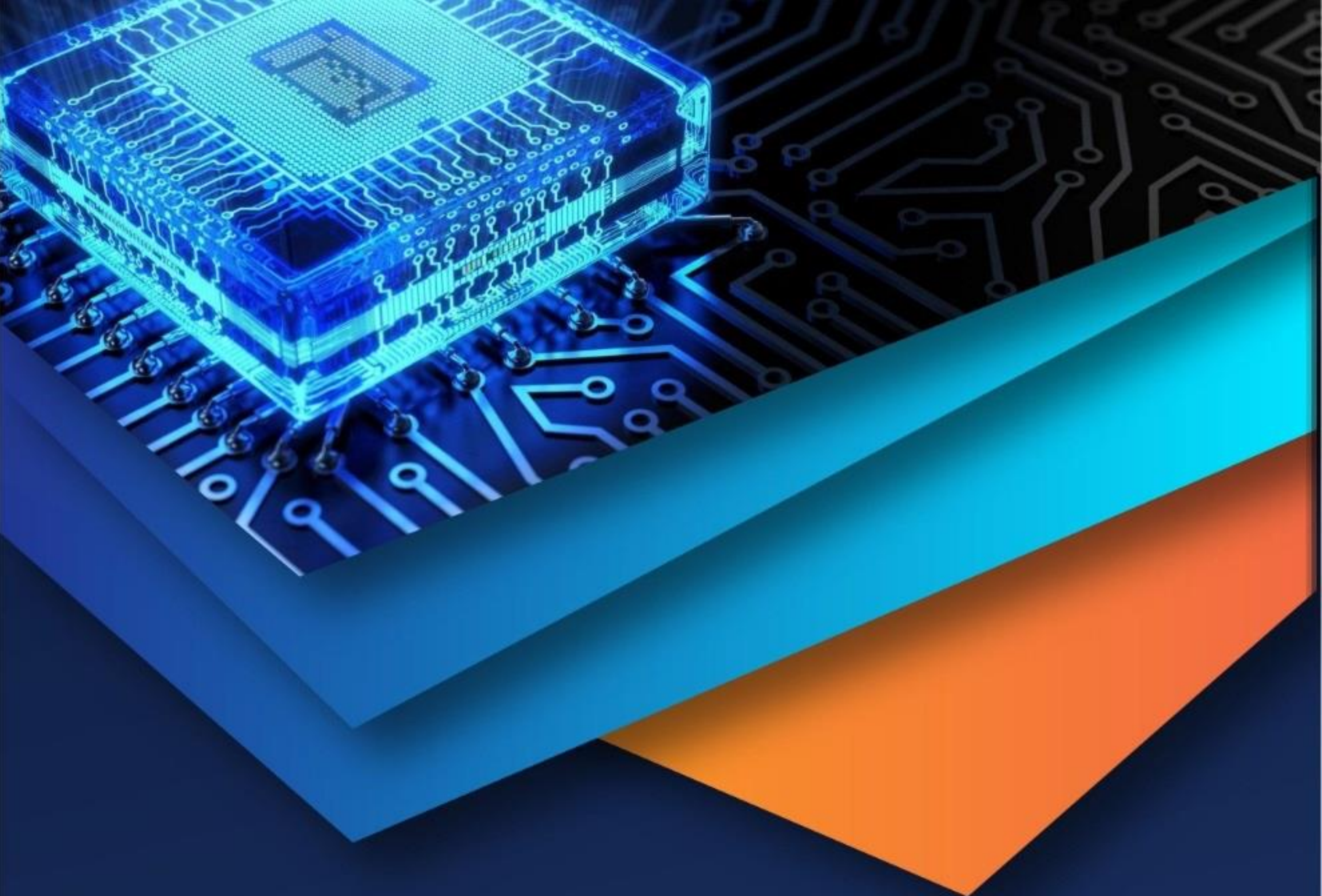

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