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A REVIEW ON CO-PYROLYSIS OF BIOMASS WITH PLASTIC WASTE: AN OPTIONAL TECHNIQUE TO OBTAIN A HIGH-GRADE PYROLYSIS OIL

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ABSTRACT

The oil produced by the pyrolysis of biomass has potential for use as a substitute for fossil fuels. However, the oil needs to be upgraded since it contains high levels of oxygen, which causes low caloric value, corrosion problems, and instability. Generally, upgrading the pyrolysis oil involves the addition of a catalyst, solvent and large amount hydrogen, which can cost more than the oil itself. In this regard, the co-pyrolysis technique offers simplicity and effectiveness in order to produce a high-grade pyrolysis oil. Co-pyrolysis is a process which involves two or more materials as feedstock. Many studies have shown that the use of co-pyrolysis is able to improve the characteristics of pyrolysis oil, e.g. increase the oil yield, reduce the water content, and increase the calorific value of oil. Besides, the use of this technique also contributed to reduce the production cost and solve some issues on waste management. This article tried to review the co-pyrolysis process through several points of view, including the process mechanism, feedstock, the exploration on co-pyrolysis studies, co-pyrolysis phenomena, characteristics of byproducts, and economic assessment. Additionally, several outlooks based on studies in the literature are also presented in this paper.

Keywords Co-pyrolysis, Pyrolysis, Feedstock and Calorific value

1.0 INTRODUCTION

The decrease of fossil fuel resources such as coal, petroleum, and natural gas has encouraged research to develop new approaches to find or invent renewable fuel. One article has predicted that the coal reserves will be available until at least by the year 2112, and it will be the sole fossil fuel in the world after 2042 (Shafee and Topal, 2009). Several efforts are currently underway to find alternative energy sources and develop technologies which have high efficiency and are environmentally- friendly. In this regard, most of the effort has been contributed by research into biomass energy. During the last three decades, more than half of the global research has been focused on biomass as renewable energy (56%), followed by solar energy (26%), wind power (11%), geothermal energy (5%), and hydropower (2%) (Manzo et al., 2013). The high percentage of research into biomass energy can be supported by the availability of biomass resources which are the world’s largest sustainable energy source and represent approximately 220 billion dry tons of annual primary production (Moreira, 2006). Beside the effect of decreasing of fossil fuels, environmental concerns also play an important role in the development of renewable energy. The risk and reality of environmental concerns have drastically increased globally and become more apparent during the past decade, particularly after Earth Summit '92 (Agarwal, 2006). To minimize environmental concerns, it is necessary to consider controlling the pollutant emissions. The optimal use of renewable energy resources can be an optional solution since it significantly contributes to decreasing the negative environmental impacts, reducing the dependence on the use of fossil fuels, and is followed by an increase of net employment and the creation of export markets (Manzo et al., 2013).

Biomass is widely accepted as a potential source of energy and is the only renewable energy source that can be converted into several types of fuels, including liquid, char, and gas, which also promise flexibility in production and marketing. Pyrolysis is generally chosen as a recommended process to achieve this goal. This process has received more attention recently because it can produce the highest liquid yield of up to 75 wt% with conditions of moderate temperature (500ºC) and short hot vapor residence time (-1 s) (Bridgewater, 2006; Ceulian et al., 2009). Nevertheless, the yield of other products also can be optimized by adjusting the parameters of operating conditions. The liquid from the pyrolysis process is known as pyrolysis oil or bio-oil, and has potential as use for fuels or feedstock for many commodity chemicals. In terms of fuels, Bridgwater et al. (1999) noted that without an upgrading process, the oil can be directly used in many applications including boilers, furnaces, diesel engines, and turbines for the generation of electricity. In addition, the greatest advantage of pyrolysis oil compared with fossil fuel is that the use of this oil has received positive comments as a more environmentally-friendly fuel because it contributes minimally to the emission of greenhouse gases (Vitolo et al., 1999).

Despite the oil from pyrolysis being environmentally-friendly, the fuel characteristic of it remains lower than fossil fuel, especially with regard to combustion efficiency. In this case, the high composition of oxygenated compounds in pyrolysis oil is responsible for this problem. Several researchers have reported that oil from the pyrolysis of biomass generally contains an oxygen content of around 35–60 wt% (Bridgewater, 2006; Athikoski, 2008; Oasma and Czemik, 1999; Parihar et al., 2007). It can be identified in the form of more than 200 different compounds in the oils, and is mostly found as water (Oasma and Czemik, 1999). However, the high level of oxygen in pyrolysis oil creates a low calorific value, corrosion problems and instability (Bridgewater, 2012).

2.0 IMPORTANCE OF THE CO-PYROLYSIS PROCESS

Simplicity and effectiveness are especially important in developing a technique to produce the ideal synthetic liquid fuel. In this regard, the idea of co-pyrolysis of biomass can be an optional technique that shows promise by meeting these two criteria. Co-pyrolysis is a process which involves two or more different materials as a feedstock. Many studies have shown that the co-pyrolysis of biomass has successfully improved the oil quantity and quality without any improvement in the system process. In contrast to catalytic cracking and HDO, co-pyrolysis has shown promise for future application in industry because of its attractive performance/cost ratios.

The successful key of this technique mainly lies with the synergistic effect which comes from the reaction of different materials during the process. A previous study has shown that the yield of oil obtained from incorporating plastic was higher than that obtained with woody biomass alone and also had a higher calorific value, which comes from hydrocarbon polymers consisting of paraffins, isoparaffins, olefins, naphthenes and aromatics, and a non-condensable gas with a high calorific value (Toba et al., 2011).

The idea of blending oil from biomass with oil from plastic seems impossible, and may increase operation costs. Oil from biomass cannot be completely mixed with oil from plastic or waste tire because of the polar nature of pyrolysis oil of biomass. If these oils are mixed together, an unstable mixture forms, which breaks (phase separation) after a short period of time. If pyrolysis of biomass and plastic waste occurs independently or separately more energy is required and the cost for oil production will significantly increase. The co-pyrolysis technique is found to be more reliable to produce homogenous pyrolysis oil than the blending oil method. The interaction of radicals during the co-pyrolysis reaction can promote the formation of a stable pyrolysis oil that avoids phase separation (Martinez et al., 2014).

Furthermore, the main benefit of using co-pyrolysis method is the fact that the volume of waste can be reduced significantly as more waste is consumed as feedstock. It also has the added benefits of reducing the landfill needed, saving costs for waste treatment, and solving a number of environmental problems. Since the disposal of waste in landfills is undesirable (Garfoth et al, 2014), this method could be proposed as an alternative waste management procedure for the future that will have a significant impact on waste reduction and may enhance energy security. In addition, from an economic point of view, co-pyrolysis has been found to be a promising option for a biomass conversion technique to produce pyrolysis oil. Kuppens et al. (2010) investigated the economic consequences of the synergetic effects of flash co-pyrolysis. They concluded that the use of co-pyrolysis techniques is more profitable than pyrolysis of biomass alone and that it also has potential for commercial development.

3.0 MECHANISM OF THE CO-PYROLYSIS PROCESS

The mechanisms of co-pyrolysis and normal pyrolysis are almost the same. Basically, the process is performed in a closed reactor system with moderate operating temperatures and in the absence of oxygen. For the purposes of oil production, there are three basic steps required for the co-pyrolysis process: preparation of samples, co-pyrolysis, and condensation. Figure 1, illustrates the steps used in co-pyrolysis to produce oil. Prior to co-pyrolysis, the samples should be dried and ground. The drying process can be performed using the oven method (temperature at 105ºC for 24 h). For industrial application, the heat demand for feedstock drying can be covered by internal heat sources through process integration. Researchers suggested that the byproducts char or gas can be combusted to provide the necessary heat for endothermic pyrolysis and other intermediate processes, such as biomass drying (Vendebosch and Prins, 2010; Veses et al., 2012). The main aim of the drying process is removing the moisture content of sample. High moisture content in feed results in the oil product having a high water content; therefore, Bridgwater (2012) suggested that the maximum moisture content in the dried feed material should be 10%. The dried samples also benefit from the grinding process, and small biomass particles with a size of less than 2-3 mm are needed to achieve high biomass heating rates (Bridgwater, 2012).

As can be seen from Fig 1, there is an optional feature in the co-pyrolysis process: inert gas. Inert gas is used to accelerate sweeping vapors from the hot zone (pyrolysis zone) to the cool zone (condenser). Short hot vapor residence times of less than 2 s are needed to minimize secondary reactions and maximize oil yield (Bridgwater, 2012). In application, nitrogen (N_2) is an inert gas that is commonly used since it is found to be cheap compared to others. Many studies have proven that the use of inert gases in the pyrolysis process has an effect on liquid yield (Demiral and Sensoz 2006; Achikogz et al., 2010)]. The proper setting of the inert gas flow rate is needed to attain maximum oil yield, while very high flow rates of inert gas actually decrease the total oil yield. However, the use of inert gas is dependent on the type of reactor used. The fluid bed reactor, circulating fluid bed reactor, and entrained flow reactor are the types which need a high flow rate of inert gas (Vamvuka, 2011). For vacuum and ablative reactors, the use of inert gas is not compulsory. Furthermore, the pyrolysis process is also influenced by many parameters, including the type of biomass, temperature, heating rate, reaction time, and particle size of feed. Detailed discussions of the effect of parameters on optimum oil yield in the pyrolysis of biomass have been thoroughly reviewed by Akhtar and Amin (2012). For co-pyrolysis, as a general rule, temperature can be adjusted within the range of 400–600ºC to maximize the production of oil. In this temperature range, more than 45 wt% oil can be produced. However, the optimum temperature required to produce the maximum oil yield is dependent on the characteristics of feedstock. Therefore, characterization with regard to thermogravimetric analysis should be performed to obtain an overview of the thermal behavior of material (Velghe et al., 2011).

Condensation is an important step in the production of pyrolysis oil. Without this step, only the char and gas products can be obtained from the process. The vapors generated during the process pass through the condensation unit to change the physical state of matter from the gas phase into the liquid phase. Vapor product residence time in the reactor can be controlled by the addition of inert gas. Bridgwater (1999) noted that pyrolysis vapors can be characterized as a combination of true vapors, micron-sized droplets and polar molecules bonded with water. Rapid cooling of the pyrolysis vapors is required to produce a high liquid yield. The lower vapor temperature (<400ºC) leads to secondary condensation reactions and the average molecular weight of the liquid product decreases. Thus, the temperature in pipelines from the pyrolysis unit to the condensation unit should be maintained at >400ºC to minimize liquid deposition; also, blockage of the equipment and piping system should be avoided (Bridgewater et al., 1999).

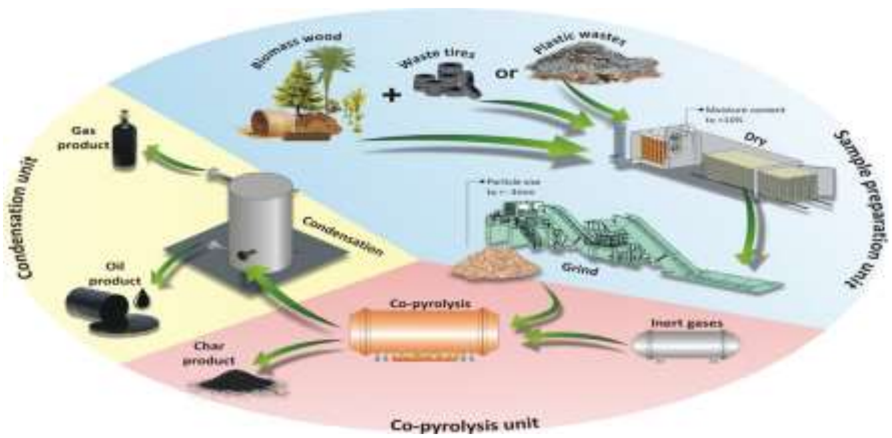

Figure 1: Co-pyrolysis of biomass

4.0 FEEDSTOCKS FOR THE CO-PYROLYSIS PROCESS

A diversity of renewable energy resources can be found around the world, including biomass energy, wind energy, solar energy and geothermal energy. Among these, biomass is the only source of renewable energy that can produce fuels in the form of solid, liquid and gas, through assistance of the pyrolysis process. Although fuels from biomass, especially wood-based biomass, typically have a lower energy content than fossil fuels, the use of co-pyrolysis technology is improving this condition. In this section, the discussion only focused on the selection and availability of feedstock which can potentially be used in the co-pyrolysis process.

4.1. Selection of feedstock

Some types of biomass have the potential for use in the co-pyrolysis process to improve the quality and quantity of pyrolysis oil. In this regard, the selection of biomass wastes is becoming an important issue requiring study. Currently, many kinds of biomass have been successfully used as feedstock in the co-pyrolysis process in research, which can be categorized into four groups:

5.0 EXPLORATION OF CO-PYROLYSIS STUDIES

The exploration of co-pyrolysis studies is necessary in order to generate ideas with regard to producing high-grade pyrolysis oil. For this reason, many efforts have been made by researchers to explore this technique, and have revealed many interesting findings. An overview of studies of the co-pyrolysis of biomass wastes with emphasis on pyrolysis oil production is described below.

5.1. Use of plastics in co-pyrolysis

Most co-pyrolysis studies have selected plastics as one of the co-feeds, with the aim of improving the oil yield in terms of quality and quantity. The summaries of studies on co-pyrolysis of biomass mixed with plastics to produce pyrolysis oil are shown in Table 1. All of the experiments listed in Table 1 were performed without any catalysts, solvents or additional pressure. Abnisah et al. (2014) investigated the co-pyrolysis of palm shell and polystyrene (PS) to obtain a high-grade pyrolysis oil.

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Palm shell is well known as a waste generated from the palm oil mill industry, and is available in huge amounts in Nigeria; around 5.2 MT were produced in 2009. Furthermore, over 280,000 Tons of waste PS is produced annually in Nigeria, most of which is contributed by food packagers. The experimental results showed that by adding the same weight ratio of PS in the pyrolysis of palm shell, the yield of oil increased to about 61.63 wt%, while the pyrolysis of palm shell alone only yielded oil at a level of about 46.13 wt%. The high yield of oil was obtained with a process temperature of 500 ºC, a heating rate of 10 ºC/min, a reaction time of 60 min, and N_2 flow rate of 2 L/ min. Moreover, the quality of oil was improved when PS was involved in the pyrolysis of palm shell. For the pyrolysis of palm shell alone, a high heating value (HHV) of oil product was obtained, of about 11.94 MJ/kg. However, pyrolysis of palm shell mixed with PS raised the HHV of oil up to 38.01 MJ/kg. Lastly, the authors concluded that the use of palm shell and PS wastes for the recovery of liquid fuel by co-pyrolysis is the key to overcoming environmental problems stemming from the high volume of palm shell waste generated by the palm oil industry; also, it can be noted that this is an optional solution to increasing energy security in Nigeria.

The pyrolysis temperature was 500ºC with a heating rate of 10ºC/min. Liquid was found to be the main product of the experiment and yields varied from 47.5 to 69.7 wt%. The lowest liquid yield was obtained from the pyrolysis of pine cone (47.5 wt%). However, by mixing the pine cone and polymers in the same weight ratio, the liquid yield obviously increased. Furthermore, Brebu et al. also reported that the energy contents of oils from the pyrolysis of mixed materials were higher than those produced by the pyrolysis of pine cone alone.

The table below shows the summary of some researchers

Ref	**Type of Materials**		**T ºC**	**Liquid Yield (wt%)**		**E Y**	**Calorific Value (MJ/kg)**	
	Biomass	**Plastics**		**Bio mass**	**Mixture (1:1)**		**Biomass**	**Mixture Ratio (1:1)**
Abnisah et al., 2014	Palm shell	PS	500	46.13	61.63	15.5	HHV=11.94	HHV=38.01
Brebu et al., 2010	Pine cone	LDPE PP PS	500 500 500	47.5	63.9 64.1 69.7	16.16.64 22.2	GCV=nd	GCV= 46.33 GCV=45.58 GCV=46.43
Cornelissan et al., 2008	Willow	PS	450	49.71	64.24	14.5	HHV=16.10	HHV=20.22
Cornelissan et al., 2008	Willow	PS	450	48.85	51.30	2.45	HHV=16.13	HHV= 18.49
Onal et al., 2012	Potato skin	HDPE	500	23.00	39.00	16.0	HHV=32.00	HHV=45.61
Lieu et al., 2012	Fir Saw dust	WEEE	500	46.30	62.30	16.0	Not reported	Not reported

Jeon et al., 2011	Wood Chip	BP	500	39.30	63.10	23.8	HHV=19.90	HHV=45.00
Jeon et al., 2011	Pine Residue	56%PE 17%PS 27%PP	400	32.00	53.00	21.0	HHV=20.00	HHV=45.00
Paredella et al., 2009	Cellulose	PS	500	45.50	58.80	13.3	Not reported	Not reported
Rutoski et al., 2006	Pinewood sawdust	PS	450	46.00	67.00	21.0	Not reported	Not reported
Jeon 2011	Willow	BP S PO S	450	50.10	52.79 59.24 51.52	2.69 9.14 1.42	HHV=16.10	HHV= 19.10 HHV= 15.70 HHV19.20

Where,

EY Extra yield, PS = Polystyrene, HDPE= High Density Polyethylene, LDOE= Low Density Polyethylene, WEEE= waste electric and electronic equipment, BP= Block Polypropylene, PP= Polypylene, Solanyl, PO S =potato starch.

Brebu et al. (2010) explored the co-pyrolysis of pine cone with synthetic polymers. The polymers used included low density polyethylene (LDPE), polypropylene (PP), and PS. In their study, pine cones were obtained from a forest in Ghana while commercial polymers of LDPE, PP, and PS were selected which were free from any stabilizers, fillers and pigments. The pyrolysis temperature was 500°C with a heating rate of 10°C/min. Liquid was found to be the main product of the experiment and yields varied from 47.5 to 69.7 wt%. The lowest liquid yield was obtained from the pyrolysis of pine cone (47.5 wt%). However, by mixing the pine cone and polymers in the same weight ratio, the liquid yield obviously increased. Furthermore, Brebu et al. also reported that the energy contents of oils from the pyrolysis of mixed materials were higher than those produced by the pyrolysis of pine cone alone.

The utilization of biopolymers in co-pyrolysis has also attracted the attention of some researchers. Cornellissen et al. have performed several studies regarding the use of biopolymers in co-pyrolysis to produce liquid fuel. Several biopolymers that have been tested include polylactic acid (PLA), corn starch, polyhydroxybutyrate (PHB), biopearls, eastar, solanyl and potato starch (Cornelissen et al., 2008a; Cornelissen et al., 2008b; Cornelissen et al., 2009). Willow was selected as a representative biomass in their study. The process was performed in a semi-continuous home-built pyrolysis reactor, flushed with nitrogen gas, and the temperature was set around 450°C (723 K). They found that the flash co-pyrolysis of willow/biopolymers blends generally results in improved pyrolysis characteristics: a synergetic increase in pyrolysis yield, a synergetic reduction of the water content in oil yield, an increase in heating value, and the production of easily separable chemicals. Among them, PHB was found to be the biopolymer with the most potential for use in co-pyrolysis since it can produce the highest oil yield and has the highest heating value.

Some interesting observations can be made from the data obtained, which are presented in Table 1. The presence of plastics in the co- pyrolysis of biomass has clearly improved the liquid yield. The pyrolysis of mixture of biomass and plastics is able to produce extra liquid, typically between 1.42 and 22.2wt%. This finding was also supported by Bridgewater, (2012) who mentioned that the increase in the yield of liquid products through co- pyrolysis may vary in the range of 2-23wt %. At the same time the energy content of the liquid represented by the calorific value showed a significant increase. Based on the data in Table 1, all types of plastics are known to improve the calorific value of the liquid product. However, the concentration of energy produced from the co – pyrolysis of bio-polymers was found to be lower compared to the oil produced from synthetic plastics.

6.0 DISCUSSION ON CO-PYROLYSIS SCENARIOS

This review showed that many researchers have studied the potency of co-pyrolysis technique using various types of biomass wastes, and that the results are very encouraging. Different investigations were conducted to obtain oil with a high yield and high quality, which followed the various available standards. Several advantages can be obtained from using this technique such as reducing the consumption of fossil fuels, solving some environmental problems, increasing energy security, and improving waste management systems. Apart from these, this technique also offers simplicity in design and feasibility in regard to economic analysis.

There are some important factors which need to be highlighted in the feed system of the co-pyrolysis process. To obtain a high grade liquid, adjustments of the types and ratios of feedstock are essential. The suitable combination of feedstock in co-pyrolysis can include wood-based biomass with waste plastic. This option is acceptable, since many studies have proven that these combinations can provide improvements in the pyrolysis oil through synergistic effects.

However, it should be noted that not all plastic types can be used in the process. PVC is not recommended as a feedstock material because it contains about 57% chlorine by weight, which will affect the diesel quality and can produce chlorinated hydrocarbons, and also because it thermally decomposes to hydrochloric acid, which is very corrosive and toxic. The presence of 1–3% PVC in the feedstock stream results in the fuel oil product having a total chloride level of 5000–10000 ppm (Scheirs, 2006).

Furthermore, it is important to note that the main aim of the addition of plastic waste in the pyrolysis of wood-based biomass is to improve the quantity and quality of the oil produced. Hence, plastic can be called the additive material in the process. In this regard, the proportion of additive material was designed to be less than that of the main feedstock (wood-based biomass). Many studies have shown that a higher ratio of additive material in the pyrolysis of wood-based biomass can contribute to increase the oil quality. However, the minimum use of additive material in each process of co-pyrolysis is preferred; this is due to some considerations such as:

– The production of waste plastics in many countries is generally found to be lower than the generation of wood-based biomass. Thus, the limited source of additive material is expected to be used and should be sufficient for the amount of wood-based biomass available.

– Besides being used as the additive material in co-pyrolysis, some wastes are also needed for the recycling process. This strategy will provide a benefit of reducing the consumption of fresh raw materials for the production new plastic, which leads to saving fossil fuel.

Co-pyrolysis is a promising technique that can produce a high grade pyrolysis oil from biomass waste. This technique also offers several advantages on its application:

– Co-pyrolysis can be easily applied to existing plants of the pyrolysis of biomass.

– Low cost associated with upgrading processes from pyrolysis to co-pyrolysis: if a plant is run for the pyrolysis of wood-based biomass, no money needs to be invested in a special plant for the use of waste plastics.

No special equipment needs to be designed and constructed for co-pyrolysis. Some minor modifications maybe needed, but only for the feed preparation system.

– As a byproduct, solid fuel is sometimes poor in organic matter; the addition of waste plastics and to wood-based biomass may improve its quality.

– The quantity and quality of desired products (oil, solid, or gas) can be easily controlled by adjusting the process parameters.

– The primary disadvantage of co-pyrolysis lies in the biomass preparation unit. Given that this technique deals with many types of biomass, an additional pre-treatment system is required, which can substantially increase the cost for the installation and operation of such units.

7.0 CONCLUSION

This review has focused on the study of co-pyrolysis techniques to produce high grade pyrolysis oil. The studies in the literature have been used to support the analysis and discussion in this paper. Many researchers have recognized that the co-pyrolysis technique can significantly improve the quantity and quality of pyrolysis oil without the presence of any catalysts or solvents and free hydrogen pressure. Therefore, this technique can be considered a simple, cheap, and effective method to obtain high-grade pyrolysis oil. Moreover, this technique also benefits to increase the calorific value of char and gas as byproducts of co-pyrolysis. As the additive material in co-pyrolysis, the availability of plastic waste and tire waste is plays an important role in the sustainability of this technique. From an economic point of view, co-pyrolysis is found to be a promising option in biomass conversion to produce pyrolysis oil. Due to the fact that biomass wastes are easy to find and available in abundant amounts around the world, co-pyrolysis has huge potential for development in many countries. In addition, by using this method, the volume of biomass wastes can be easily controlled. Using biomass wastes to produce pyrolysis oil could reduce the need for landfills, decrease the cost of waste treatment, and solve some environmental problems. Furthermore, it can also be noted that this is an optional solution to increase energy security of the nation and reduce dependence on fossil fuels.

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