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Pyrolysis oil an emerging alternate fuel for future (Review)

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Abstract
The demand and prices of the available petro fuels is increasing with time. So, it has become a point of attention for the researchers to find alternative fuels to fulfil the future requirement of petro fuels. Due to serious issue globally and in India on the use of fossil fuels, it is necessary for India to start using renewable energy sources. There are lots of waste available in India from various sectors like biomass from agriculture and forests; industrial waste, plastic waste and scrap tyres etc. There is an urgent need to utilize such wastes for producing alternate fuels by using proper technique and methodology. In India about 686 MMT gross crop residue biomass is produced annually. Also, plastic products have become an integral part in our daily life as a basic need and is produced on a massive scale worldwide and its production crosses the 150 MMT per year globally. In India approximately 8 MMT plastic products are consumed every year. Approximately 5.6 MMT per annum plastic waste is generated in the country, which is about 15342 tons per day. Also, India is the third largest producer, fourth largest consumer of natural rubber and fifth largest consumer of synthetic rubber. Globally, it is estimated that 13.5 MMT of tyres are scrapped every year. In India about a million tonnes of scrap tyres are available annually. Globally it is a major environmental concern to dispose the waste tyres. Efforts are going on by researchers to produce an alternate fuel by using such waste. At some places in the country pyrolysis oil i.e. bio-oil is produced from such wastes by using a pyrolysis technology. Since, the obtained pyrolysis oil has certain properties close to the high speed diesel, it is therefore necessary to compare the fuel properties of pyrolysis oil with high speed diesel for its direct or modified use in CI engines.

Keywords: Energy Sources, Pyrolysis Oil, Fuel Properties, Alternative Fuels, Waste Tyres

Introduction

The prices of the petro fuels are increasing at a high rate so it has become necessary to develop the alternate renewable fuels. Use of renewable fuels not only save environment but also contribute to economy of the country. The pressure is increasing day by day due to rising fuels prices, diminishing global supplies of crude oil and legislation to control climate change which resulted in aggressive renewable fuel policies and a rapid growth in the emerging bio fuel industry. The awareness about the environmental issue is increasing day by day thats why the pressure for environmental sustainability and implementation of the various strategies is mounting on organization to reduce environmental impact of their product and waste. India is the country in which there is lots of waste available every year from various sector like agriculture and industrial waste. Therefore, it has become necessary to think about the utilization of such wastes for producing alternate fuels through proper upgradation processes and technique.

India is one of the developing countries whose economy is largely based on agriculture. It constitutes the backbone of rural India whose inhabitants are more than 70% of total population. As a result, lots of agricultural wastes are generated and remain unutilized. In India around 60.47 percent land area is under agriculture which produces about 686 MT gross crop residue biomass annual bases. Globally, 140 billion metric tons of biomass is generated every year from agriculture. This available biomass can be converted in to large amount of energy and also to get some by products. It is estimated that around 50 billion tons of oil and agricultural biomass waste transformed to energy. This energy can significantly replace fossil fuel, decrease emissions of greenhouse gases and supply renewable energy to around 1.6 billion people in developing countries, which still lack access to electricity. As raw materials, biomass wastes have striking potentials for large-scale industry and community-level enterprises [1].

Now days plastic product have become unavoidable part of human life. Its production is increasing day by day on large scale which crosses the 150 million tonnes per year globally. It is estimated that every year in India around 8 MMT of plastic products are utilized.

It is broadly used for various application likes in films, plastics bags, wrapping materials, fluid containers, clothing, toys, household, industrial products and building materials. It is well known that plastic is non degradable and it will remains on landscape for several years. Plastic can be recycled but the problem is that recycled products are environmentally more hazardous than virgin product. Also, there is some limitation in recycling the base product because the plastic material get deteriorate after every recycling due to thermal pressure. Hence, it can be done only 2-3 times. It is estimated that approximately 70% of plastic consumption is converted as waste and around 5.6 MMT per annum plastic waste is generated in country, which equals to 15342 tons per day [2]

Another area in which there is need to pay attention for waste management is rubber waste generation. India rank three in the production and fourth largest consumer of natural rubber. Also, fifth largest consumer of synthetic rubber. Indian Rubber Industry plays a very vital role in the Indian national economy. It is estimated that 13.5 MMT of tyres are scraped globally from which 40% comes from the emerging market likes India, Southeast Asia, China, India, South America, South Africa and Eastern Europe. In India about millions tons of scrap tyres are available annually. This figure is increasing at very high rate as the number of vehicles is increasing in various sectors and abuts to reach the Wastern level. It has become a major issue to dispose the waste tyres which has become a major environmental concern globally. The main reason for this is that increasing use of automobile as well as population especially in the industrialized nations. The main reason for the problem cause by waste tyre is that it is not biodegradable and if there is no proper management it remains in the same state for several decades [3]. Researchers are doing efforts to produce an alternative fuels from such waste. At some part of country through the pyrolysis processes pyrolysis oil i.e. bio-oil is produced from such waste. It is observed that the obtained pyrolysis oil has certain properties close to the high speed diesel. Hence, It is necessary to compare these obtained pyrolysis oil with high speed diesel based on their fuel properties to ascertain its use as fuel in constant speed CI engines.

Pyrolysis processes

Pyrolysis is the chemical decomposition of condensed organic substances by heating. The word is coined from the Greek-derived elements pyro "fire" and lysis "decomposition". Pyrolysis is usually the first chemical reaction that occurs in the burning of many solid organic fuels, like wood, cloth, and paper, and also of some kinds of plastic. Anhydrous pyrolysis can also be used to produce liquid fuel similar to diesel from plastic waste. Depending on the operating condition, pyrolysis can be classified into three main categories: conventional, fast and flash pyrolysis. These differ in process temperature, heating rate, solid residence time, biomass particle size, etc. However, relative distribution of products is dependent on pyrolysis type and pyrolysis operating parameters as shown in Table 1. In addition, different types of pyrolysis processes are described in the following three sub-sections.

Table 1: Typical operating parameters and products for pyrolysis process [4, 5]

Pyrolysis Process	Solid Residence Time (s)	Heating Rate (^{0}K/s)	Particle Size (mm)	Temp. (^{0}K)	Product Yield (%)		
					Oil	Char	Gas
Slow	450–550	0.1–1	5–50	550–950	30	35	35
Fast	0.5–10	10–200	<1	850–1250	50	20	30
Flash	<0.5	>1000	<0.2	1050–1300	75	12	13

Slow Pyrolysis

Slow pyrolysis has been used for thousands of years to enhance char production at low temperatures (550-950 ^{0} K) and low heating rates between 0.1-1 ^{0}K/s. [4, 5] In this process, the vapour residence time is too high and may range between 5 min to 30 min. The components during the process are in the vapour phase which continues to react with each other resulting in formation of solid char and other liquids[6]. However, slow pyrolysis has some technological limitations which made it unlikely to be suitable for good quality bio-oil production. Cracking of the primary product in the slow pyrolysis process occurs due to high residence time and could adversely affect bio-oil yield and quality. Moreover, long residence time and low heat transfer demands extra energy input [7, 8].

Fast Pyrolysis

In the fast pyrolysis process, biomass is rapidly heated to a high temperature (850–1250 ^{0}K) in the absence of oxygen and residence time between 0.5–10 s [4, 5]. Typically on a weight basis, fast pyrolysis produces 60%–75% of oily products (oil and other liquids) with 15%–25% of solids (mainly biochar) and 10%–20% of gaseous phase depending on the feedstock used. The production of liquids is usually yielded from biomass in a low temperature, high heating rate and short resident time environment. The basic characteristics of the fast pyrolysis process are high heat transfer and heating rate, very short vapour residence time, rapid cooling of vapours and aerosol for high bio-oil yield and precision control of reaction temperature [9]. Fast-pyrolysis technology is receiving incredible popularity in producing liquid fuels and a range of speciality and commodity chemicals. This liquid product can be easily and economically transported and stored, thereby de-coupling the handling of solid biomass from utilization [10]. It also has potential to supply a number of valuable chemicals that offer the attraction of much higher added value than fuels. Fast pyrolysis technology can have relatively low investment costs and high energy efficiencies compared to other processes, especially on a small scale [11, 12]

Flash Pyrolysis

The flash pyrolysis of biomass is a promising process for the production of solid, liquid and gaseous fuel from biomass which can achieve up to 75% of bio-oil yield[13]. This process can be characterized by rapid devolatilization in an inert atmosphere, high heating rate of the particles, high reaction temperatures between 450 °C and 1000 °C and very short gas residence time around less than 1 s [14]. However this process has some technological limitations, for instance: poor thermal stability and corrosiveness of the oil, solids in the oil, Increase of the viscosity over time by catalytic action of char, alkali concentrated in the char dissolves in the oil and production of pyrolytic water [15].

Pyrolysis Process for Different Feedstocks.

Biomass pyrolysis process

The process of pyrolysis of organic matter is very complex and consists of both simultaneous and successive reactions when organic material is heated in a non-reactive atmosphere. In this process; thermal decomposition of organic components in biomass starts at 350 °C–550 °C and goes up to 700 °C–800 °C in the absence of air/oxygen. The long chains of carbon, hydrogen and oxygen compounds in biomass break down into smaller molecules in the form of gases, condensable vapours (tars and oils) and solid charcoal under pyrolysis conditions. Rate and extent of decomposition of each of these components depends on the process parameters of the reactor (pyrolysis) temperature; biomass heating rate; pressure; reactor configuration; feedstock; etc [16]. The crude pyrolysis oil obtained through this process is black coloured fluid generally called as bio-oil or pyrolysis oil. The other main product of this process is slurry which can be made from charcoal and waste by adding some chemical for stabilization. Slurries can also be made from the oil and charcoal. In general case liquid products are easier to control in combustion process and this thing is important with the view to modify the existing equipment. The available oil fired burners are not able to use directly solid biomass without modification. But, the pyrolysis oil, char-oil slurry and char-water slurries required very minute modification of the equipment or even existing cab be use as available. As a partial fuel replacement in coal powered burners can easily accept charcoal until the volatile content is compatible with the design of burner. The bio-oil and slurry fuels with the addition of little amount of alkali ash in the char gas turbines can be readily fired in the power station. The pyrolysis oil after the upgradation can be use in the engine without any modification. For the leisure and industrial application there is a market for charcoal lumps and briquettes in some countries.

Plastic pyrolysis process

The pyrolysis process for plastic takes the long chain polymer molecules and breaks or cracks them into shorter chains through heat and pressure. Essentially the process is same the natural process of the earth to break down carbon into oil which takes million of years in nature. The pyrolysis process does this with intense heat in a closed system in a short amount of time. Conditions for producing pyrolysis oil are more likely to include virtually no oxygen. The pyrolysis of plastics produces a liquid product, pyrolysis oil or oil that can be readily stored and transported.

Plastic pyrolysis process is the thermal de-polymerization process in the absence of oxygen which is able to convert plastic into gasoline-range hydrocarbons [17]. The waste plastic used in pyrolysis process is needed to be sorted and cleaned. The Polyethylene (PE) and Polypropylene (PP) which are the main component of the plastic in municipal solid waste are used in the process in order to prevent the contamination of chlorine in the oil [18]. The classified waste plastic is processed from an autoclave pyrolysis reactor. In general, product yields from pyrolysis are varied with temperature. The plastic pyrolysis oil used in this research is processed at 300-500 °C t atmospheric pressure for 3 hours. The product output consists of 60-80% pyrolysis oil, 5-10% residue and the rest is pyrolysis gas on weight basis

Tyre pyrolysis process

One of the best methods of dispose is pyrolysis of scrap tires. Pyrolysis offers an environmentally and economically attractive method of waste tires transformation into useful products and energy. Pyrolysis also represents one of the most important steps during the waste tire gasification. Thermogravimetry analysis reveals that the pyrolysis of tire rubber at atmospheric pressure starts at a temperature around 250 ºC and finishes at a temperature of about 550 ºC. Generally, more than one degradation temperature region during rubber pyrolysis is recorded. In general, by pyrolyzing waste tire, three fractions are obtained: solid residue (around 40 wt. %), liquid fraction (around 50 wt. %) and gas fraction (around 10 wt. %). The general trend is an increase in yields of liquid and gas fractions as the temperature increases. From the works devoted to tire pyrolysis, which are focused on the generation of liquid fuel results that derived liquids are a complex mixture of organic compounds containing a lot of aromatics. This liquid can be separated into lighter and higher fractions [19].

Composition of Pyrolysis oil

Biomass pyrolysis oil

Mullen and Boating while comparing the different crops bio oil gave the elemental analysis as shown in Table 2. The ash content of the biomass samples is much higher for both of the alfalfa stems than it is for the switchgrass, and ash content is higher for the less mature alfalfa stems. This is significant because alkali metals contained in the ash have been shown to be catalysts for changing the depolymerization mechanisms during pyrolysis leading to changes in the composition of pyrolysis products.The percentage of fixed carbon was also found greater in the alfalfa stems than in the switchgrass samples, resulting in the switchgrass containing >10% more volatile matter than the alfalfa stems. The elemental analysis reveals that the nitrogen content is much greater for the alfalfa stems than for switchgrass as would be expected because alfalfa is a nitrogen fixing legume. The nitrogen level were higher in the alfalfa stems at the early bud stage [20]

Table 2: Elemental Analysis of Bio-Oil [20]

S.N.	wt %, db	Switchgrass	Alfalfa, early bud	Alfalfa, full flower
1.	C	47.47	53.88	56.84
2.	H	6.96	8.47	7.86
3.	N	0.36	4.59	3.73
4.	S	-a	0.05	0.07
5.	CI (ppm)	-a	249	242
6.	O	45.19	32.73	31.30
7.	ash	0.01	0.28	0.30

Note: -a = not determined

Tyre and Plastic Pyrolysis oil

The waste plastic used in pyrolysis process is needed to be sorted and cleaned. The Polyethylene (PE) and Polypropylene (PP) which are the main component of the plastic in municipal solid waste are used in the process in order to prevent the contamination of chlorine in the oil. [21] The plastic pyrolysis oil used in this research is processed at 300-500 °C at atmospheric pressure for 3 hours. The product output consists of 60-80% pyrolysis oil, 5-10% residue and the rest is pyrolysis gas on weight basis. Pyrolysis is a complex series of chemical and thermal reactions to decompose or depolymerize organic material under oxygen-free conditions. The products of pyrolysis include oils, gases and char. The pyrolysis oil products in this research are from tire and plastic which are dissimilar in physical properties and chemical properties. The appearance of the tire pyrolysis oil is thick-liquid and dark colour oil whereas the appearance of the plastic pyrolysis oil is like grease oil and dark colour oil at 30°C (room temperature). They all strong smell due to the high aromatic substance. As the comparison usage of this research is in diesel engine, the pyrolysis oil from process is a mixture of carbon composition which are C5-C20 in tire pyrolysis oil and C10-C30 in plastic pyrolysis oil [22].

Pyrolysis of scrap tyres produced oil similar in properties to a light fuel oil, with similar calorific value, sulphur and nitrogen contents. The oil was found to contain 1.4 % sulphur and 0.45 % nitrogen on mass basis and have similar fuel properties to those of diesel fuel. The oils contained significant concentration of polycyclic aromatic hydrocarbons some of which have been shown to be either carcinogenic and or mutagenic. A single oil droplet combustion study was carried out and also the oil was analysed in detail for its content of polycyclic aromatic hydrocarbons (PAH). The derived oil was combusted in an 18.3 kW ceramic-lined, oil-fired, spray burner furnace, 1.6 m in length and 0.5 m internal diameter. The emissions of NO_x, SO_2, particulate and total unburned hydrocarbons were determined in relation to excess oxygen levels. Throughout the combustion tests, comparison of the emissions was made with the combustion of diesel. The concentration of PAH increased from 1.5 to 3.4 wt. % of oil as the pyrolysis temperature increased from 450 to 600°C. The formation of PAH was attributed to a Diels–Alder type mechanism involving cyclisation of alkenes and dehydrogenation to form aromatic hydrocarbons. A range of potentially high value volatile hydrocarbons was identified in significant concentrations in the oils. It was found that tyres pyrolysed at 475°C found to be optimum pyrolysis temperature and the Tyre pyrolysis temperature at this temperature has the chemical composition by % wt are: Carbon (84.6 %), Hydrogen (11.2), Nitrogen (0.5 %), Sulphur (1.4 %), Ash (0.002 %) and Oxygen by difference (2.2 %) [23].

Properties of pyrolysis oil as fuel

The fuel properties of pyrolysed oil from different feedstock i.e. tire, plastic and biomass as well as that of diesel fuel given by different researcher is shown below in the Table 3. The tyre oil and plastic oil has very near calorific value to diesel fuel. Tire oil has maximum carbon percent where as maximum value for percent of hydrogen was found in the plastic pyrolysis oil. The percent oxygen value found very low in plastic pyrolysis as compare to others two but it was found highest in case of biomass pyrolysis oil. Value of sulphur content was less than 0.05 percent in typical biomass oil while it was less than or equal to 1 in case of tire oil. The density of tyre and plastic pyrolysis oil has nearly equal to diesel fuel while it was slightly high in case of biomass pyrolysis oil. Viscosity and flash point has also near values to diesel fuel.

Table 3: Properties of pyrolysis oil.

Properties	Tire Pyrolysis Oil [24]	Plastic Pyrolysis Oil [24]	Typical Biomass Pyrolysis Oil [8, 25]	Diesel Oil [24]
Heating Value (kJ/kg)	43,225.9	46,199.12	n.a	45,814.74
C (%)	84.67	83.79	47.47	87
H (%)	10.44	11.36	6.96	13
O (%)	4.17	2	45.19	n.a
Cl (%)	n.a	0.03	n.a	n.a
S (%)	≤1	n.a	<0.05	n.a
Density @ 30°C (g/cc)	0.924	0.8147	1.10–1.30	0.7994
Viscosity @ 40°C (cp)	2.69	2.49	n.a	1-4.11
Flash Point (°C)	68	100	40–110	70

n.a – not determined

Conclusion

It is evident from the past research that pyrolysis process is very successful in producing the pyrolysis oil from different feedstock. The pyrolysis oil has the fuel properties havng some similarities with the diesel fuel. The calorific values for tyre and plastic pyrolysis oil were observed as 43225.9 and 46199.12 kJ/kg respectively which are approximately equal to diesel fuel that i.e. 45814.74 kJ/kg. Also, the viscosities for tyre and plastic oil were determined as 2.69 and 2.49 cP respectively which were in the range of viscosity between 1-4.11 cP observed for diesel. The flash point for tyre and plastic pyrolysis oil was observed as 68 and 100 ^{0}C which were nearly equal to diesel fuel i.e. 70 ^{0}C in case of tyre oil while it was slightly high for plastic pyrolysis oil. The flash point for typical biomass oil was in the range between 400-110 ^{0}C which includes the value of flash point for diesel [8, 24, 25]. Also there is need to upgrade the pyrolysis oil for engine use as fuel by the upgradation techniques like vacuum distillation, thermal cracking, blending, microemulsion Etc. also there is need some research to find out the advanced upgrading method so that pyrolysis oil can be seen as a very promising alternative fuel in future.

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