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BIOFUELS FROM BIOMASS

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ABSTRACT

Biomass is the most abundant, renewable unexplored source of energy. It is organic in nature, basically comprising cellulosic in nature and hemicellulosic matter found in the bio-degradable material from energy crops , agricultural and forest wastes , industrial, consumer and animal wastes . Energy reach compounds, otherwise known as bio-fuels, are prepared from the bio-mass by three important processes, physical, biological and thermo-chemical process. Bio-fuels are prepared in three forms that are solid, liquid and gaseous. Since these bio-fuels are the products from the bio-mass or the biological wastes as mentioned above, so bio-fuels draws credits for re-circulation of carbon to the atmosphere, rather adding more of Green House Gas. This also contains very less amount of sulphur compounds so SOx pollution is negligible. It is also seen, that nitrogen content in bio-flues compared to fossil fuels is less to 50%, resulting low NO_x release to atmosphere. These are the basic reasons why this plays an advantageous role than the fossil fuels to bring back a healthy environment by restricting the Green House Effect, which is of great concern.

INTRODUCTION

Biomass is the most abundant and renewable resources of energy in the world. It is any organic matter, particularly cellulose or hemicellulosic matter, which is available on a renewal basis or recurring basis, including trees, plants and associated residues, poultry litter and other animal waste, industrial waste and the paper components of municipal solid waste.

With the depletion of fossil fuels and the global Green House Effect, renewable energy is validating its position and importance in the field of energy by fulfilling the requirement environmentally and also as a source for renewable energy. With it zero emission of CO_2, biomass is one of the most, potentially rich resource of energy that is to be explored. Biomass is converted into bio-fuels using different processes mostly because biomass is a low energy density material with a low bulk density, it degrades on storage and also it is difficult and costly to transport, store and use. The cellulose are dehydrated glucose units with a degree of polymerization of 10,000, where as hemi cellulose are linear polymers of C_5 and C_6 compounds with degree of polymerization of less than 200. Lignin is a random three-dimensional structure of phenolic compounds.

Bio-fuels from Biomass: -

The parameters like temperature conditions, volatility, reactivity and pressure effect the depolymerization of the biomass to gas through decomposition process and many complex reactions. The biofuels obtained from different biomass are classified into solid, liquid and gases.

SOLID BIOFUELS: -

They are solid biomass that are combustible such as wood, compressed peat and dry bagasses etc., these can be burnt to get heat as a form of energy.

LIQUID BIOFUELS: -

This basically consists of liquid extracted from biomass and used as fuel and for production of other useful chemicals. This liquid stream consists of bio-oils and other organic chemicals. It is dull black –brown liquid and remains in liquid form at room temperature. This contains many chemicals mainly ethanol, methanol, acetone, acetic acid, bio-oils and bio-diesel.

GASESS BIO-FUELS: -

Gaseous product obtained from biomass decomposition contains primarily hydrogen, methane, carbon monoxide, carbon dioxide, ammonia and other gases depending upon the organic nature of biomass and process condition..

CONVERSION OF BIOMASS INTO BIOFUELS

Biomass can be converted to bio-fuels by three main processes: physical, biological and thermo-chemical.

Physical process:

In this process the biomasses used are oil rich seeds. Oils are extracted from oilseeds and the extracted oil is refined by esterification with alcohol to reduce viscosity and improve the quality of bio-fuels. This bio-fuel can be used as diesel substitute, so it is known as bio-diesel.

Biological process:

In biological processes, the wet biomass is used as raw materials. The wet biomass is treated with micro-organisms in the presence or absence of oxygen for a longer time. The main products obtained in this process are bio-ethanol and biogas. Biological processes are of two types, fermentation and anaerobic digestion.

Fermentation:

Generally bio-ethanol is produced by fermentation of sugar components of biomass. Feedstock for this process are sugar cane and sugar beets, which store the energy as simple sugars; other plants, which store energy as more complex sugars like starches; cellulosic biomass,which is made up of very complex sugar polymers, etc. Complex poly saccharides are converted to simple sugars by hydrolysis. During hydrolysis acids and enzymes are used to catalyse the reaction. Then simple sugars are converted to ethanol by fermentation process using yeast or bacteria as catalyst.

Anaerobic digestion:

In this process the biomass is treated with micro-organisms like yeast in absence of oxygen to produce biogases the main product in this process is methane. Depending upon the solid content in biomass, the anaerobic digestion process is classified as dry digestion and wet digestion process. In dry digestion process solid content is 25 – 30% while in wet digestion the solid content should be less than 15%. Solid content of biomass play an important role in designing the reactor and the economy of the process.

Thermo-chemical processes:

In these processes, the feed stock is heated in the presence (or absence) of oxygen or water for a short time. The products obtained are fuel gases and bio-oils which can be upgraded by different other processes to get energy reach chemicals of various compositions. The different thermo-chemical processes are combustion, gasification, pyrolysis and hydrothermal liquefaction.

Combustion: It involves complete oxidation of carbon of biomass to CO_2, release of heat energy, which is used immediately. Thermal efficiency of this process is very low and it produces emission problem.

Gasification: Biomass can be converted to synthesis gas (consisting primarily of carbon monoxide, carbon dioxide and hydrogen) by a high temperature gasification process. The produces gases are either used in boiler or for production of valuable chemicals.

Pyrolysis

With increasing research in this field, it is seen by many researchers that fast pyrolysis is one of the area of development and with slight modification in process and process condition may give a proper methodology for conversion of biomass to biofuels inorder to make up the short comings, arising due the depletion of fossil fuels.

Pyrolysis is thermally initiated depolymerization process also known as thermolysis, which doesn't, involve any sort of oxidizing agent. Sometimes with limited supply of oxidizing agent and controlling the reaction leads to partial gasification. Pyrolysis product basically consists of gases like CH_4, CO_2, and NH_3 and liquids like ethanol, bio-oils, acetone, acetic acid etc and solid as char. The relative proportion of the output depends upon the process and process condition, characteristics of biomass, optimum temperature and residence time of material. A brief flow sheet of the pyrolysis process has been shown in fig-1. The temperature controls the quantity of gas or liquid yield. A substantial change in the proportion of gas, liquid products and char is obtained with the change in rate of heating, temperature of the reaction and residence time[3-4]. In this process the biomass is heated to a temperature range of 650^0C to 1000^0C with low residence time and rapidly cooled to collect the condensed liquid product. This is done to avoid the decomposition of the intermediate products during pyrolysis [5]. When cooled, most volatiles condense to from Bio-oil and remaining gases comprise a medium calorific value of non- condensable gases[6].

Specification of pyrolysis products:

Compared to bio-oils the gaseous products have low calorific value, which becomes hindrance for the parameters to maintain high yield of gaseous product and its utilization.

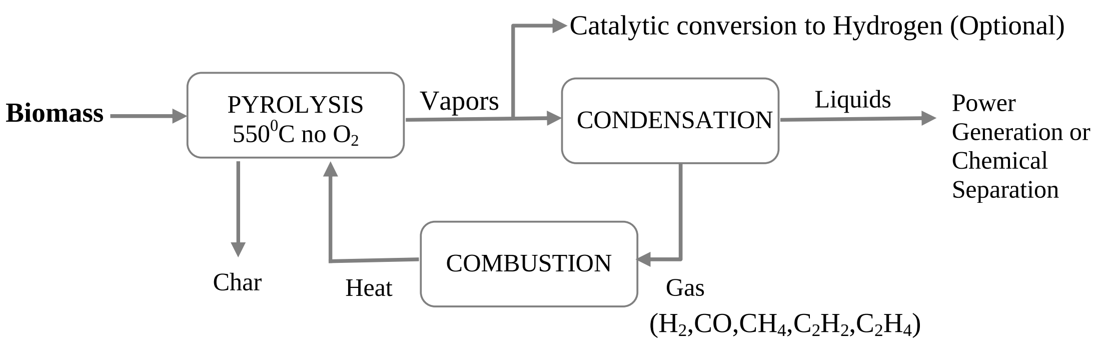

Fig-1: Pyrolysis Process of Biomass

After proper cleaning, these gaseous products can be used in gas-fired engines, turbine & fuel cells. Average %composition of gas is H_2 (12.8), CO (17.0), CO_2 (2.5), CH_4 (19.2), C_2H_4 (20.8), C_2H_6 (7.2), C_3H_6 (9.4) and C_4+ above (10.1).[7]

Bio-oil is a liquid mixture of oxygenated compounds containing various chemicals having functional groups such as carbonyl, carboxyl and phenolic. It is tasteless, odorless but due to small percentage of H_2S it has pungent odor. It solidifies when expose to air.

Bio –oil Analysis:

Bio-oil is a dark brown liquid that is free flowing with a pungent odor due to H_2S percentage. It is highly acidic and corrosive in nature. Bio-oil contains several hundred different chemicals with a wide-ranging molecular weight distribution. **Table- (2)** lists and illustrates the properties of Bio-oil produced by BioTherm[8] pilot plant derived from three different biomass feed stock. Similarly **Table (3)** illustrates typical comparison of properties of bio-oil to that of diesel [8]. Keeping in view the product concentration and the quality comparison with diesel, the data substantiate for more developmental work in the direction of upgrading the Bio-oil to make it compatible with diesel in this competitive market.

TABLE: 2 DynaMotive Bio Oil Properties:

Bio mass	Pine/Spruce 100% wood	Pine/Spruce 53% wood 47% bark	Bagasse
Moisture wt %	2.4	3.5	2.1
Ash content wt %	0.42	2.6	2.9
Bio-Oil pH	2.3	2.4	2.6
Water %	23.3	23.4	20.8
Lignin wt %	24.7	24.9	23.5
Solid Content wt %	<0.10	<0.10	<0.10
Ash wt %	<0.02	<0.02	<0.02
Density kg/lts	1.20	1.19	1.20
Calorific Value MJ/Kg.	16.6	16.4	15.4
K. Viscosity CSt @ 20^0C	73	78	57
CSt @80^0C	4.3	4.8	4.0

TABLE-3: Comparison of Bio-oil with Diesel

Parameter	Bio Oil	Diesel
Calorific Value MJ/Kg.	15.20	42.0
K. Viscosity CSt	3-9@80^0C	2.4 @20^0C
Acidity pH	2.3-3.3	5
Water wt %	20-25	0.05 V % Combined
Solid wt%	<0.1	
Ash wt %	<0.02	0.01
Alkali (Na + K) ppm	5-100	<1

Disadvantages in Bio-oil:

Pyrolytic bio-oil, having a number of draw-backs, typically its acidic nature(pH 2.5-3.4), contains substantial amount of water 20-30%, ash 0.04-0.24% and its viscosity ranging between 35 to 53 CSt at 40^0C [9]. Scott et.al[10] reported about formic acid and acetic acids in fast pyrolysis products ranges between 0.4-7.2% and 2.1-6.1% respectively depending on feeds stocks. In addition to all these , bio-oil has low calorific value than diesel because of water and oxygenates. This structural water disables it, in mixing with hydrocarbon based diesel oil. This also contains suspended char originating from pyrolysis which becomes a reason for particulate emission due to slow burning of the oil. So as produced bio-oil are difficult to use as it may corrode the delivery system and storage tank. Since there is alkali content it is believed that the oil during storage tends to polymerize making the liquid viscous. Raveendran et. al [11] has development co-relation showing the effect of lime and potassium in presence of lignin on the change in the volatile fraction.

Upgradation of biofuels obtained by pyrolysis:

Different processes have been developed for upgradation of biofuels. Emulsification of pyrolytic bio-oil in diesel fuel was done by Michio Ikura et.al.[9] . This was done to curtail the basic problem like high viscosity, highly acidic and not easily burning nature, for which the bio-oil was fractionated to heavy fraction and light fraction by centrifugation prior to emulsification. With a series of emulsification with No.-2 diesel carried to relate process condition, emulsion stability and processing cost. For this, process variables like temperature, residence time, bio-oil concentration, surfactant concentration and power input per unit volume were considered. But excluding temperature and residence time the other three variable showed significant effect on emulsion stability ,fuel properties like: heating value, cetane number , viscosity and corrosively. These variables showed reduction in heating value of the emulsions, decrease in the viscosity of the emulsion of 10-20% bio-oil compared to the original bio-oil leading the product, to be handle. Corrosively of a pyrolitic bio-oil was found to be twice that of emulsion fuels. The cetane number was found to be 5.6.

Catalytic improvement of the yield of synthesis gas was emphasized by Malekar et. al. [7]. Usually 40% (dry basis) starting raw material goes into tar formation and gas yield is in the range of 15-20% (dry basis). Here they found that the particle size during pyrolysis is an important factor to be taken care as smaller the particle size higher is yield of gaseous products. Silica alumina catalyst bed reduces the deposition of tar on furnace wall, this is because silica alumina catalyst degrades the longer chains of aliphatic and aromatic compounds into smaller hydrocarbon thereby decrease in tar formation. This as a result increases the gaseous products yield nearly 1.5 to 2.0 times than that of without catalyst. Thus H_2 and CO increases, increasing the synthesis gas yield.

Zhogyang Luo. et. al [5] used fluidized bed reactor with feed rate 20 kg/hr. Which was designed with various sections to reduce the volatile residence time for restraining secondary cracking. Reutilization of char and gas reducing the cost of heating required for the purpose. Multistage condensation was adopted for disposal of heavy oil and high water content liquid separately. This reduces the subsequent processing cost and maximizes high quality fuel oil production.

Direct Hydrothermal Liquefaction:

This process involves different process conditions as compared to pyrolysis of biomass. In this process biomass is brought into contact with water at elevated temperature (300-350^{0}C) with sufficient pressure (12-20 MPa) to keep water in liquid state with a minimum residence time up to 30 minutes, where an oily liquid separates out with reduced oxygen content nearly (10%) and water containing soluble organic compounds. For enhancement of liquefaction, alkali may be added as a catalyst for organic conversion

High Thermal Upgrading process:-

The feed stock is treated with water at temperature ranging from 300^{0}C to 360^{0}C and 100-180 bar of pressure with residence time of 5-20min. Biomass contains nearly 40-45% weight (DAF basis) of oxygen. The oxygen content leads to low calorific or heating value and removal of O_2 leads to upgradation of the oil. Now removal of O_2 can either be done in from of water or inform of CO_2. Removal of O_2 in form of H_2O leads to increase in carbon content. And removal of O_2 as CO_2 tends to leave the bio-oil with higher H/C ratio and there by increasing the LHV. After removal of O_2 as CO_2 the product left is the bio-crude, organic dissolves (OD) and gases.

Bio-crude: -This is the main product with O_2 content of 12-20% wet and H/C ratio is 1-1.3 having average molecular weight of almost 300. It is relatively high heating value (LHV is 30-35 MJ/kg). It has main application for power generation (e.g) co-combustion in coal fired power plant. Alternatively it can be upgraded by catalytic hydro-oxygenation**.**

Organic dissolved**:-**Organic fraction dissolved in the water after cooling of the reaction mixture to ambient temperature are acetic acid, acetone and components like methyl cyclopentanone and hydroxy-pyridine.

Gases: Apart from CO_2 this gas contains carbon monoxide and traces of methane and hydrogen.

Experimentations have demonstrated that in HTU process, diesel fuel with excellent properties can be prepared by Hydrodeoxygenetion process of bio-crude. Thus the HTU process is very well suited for the conversion of wet biomass feed stocks.

Upgrading biocrude of HTU process :

Biocrude obtained from HTU process contain 12-20 % wt oxygen and some impurity containing sulfur and nitrogen. In order to improve the stability and C/H ratio of bio-crude, oxygen and the impurities has to decrease and it is done by Hydrodeoxygenetion process.In this process bio-crude is treated with hydrogen at a temperature between 200 to 450^0C and pressure between 30 and 150 bar over a catalyst Co Mo/ - Al_2O_3 for a residence time of 10-20 minutes. The products obtained are Naphtha, Kerosene, Gas oil and 370^0C fraction. Oxygen content of product is below 0.1 %.

Comparison of bio-oil with diesel for typical parameters is given in table (3). Bio-oil has a number of environmental advantages over fossil fuels.

Bio-mass degrades rapidly releasing the elements like C, N, O_2, H_2 to the atmosphere. The bio-oil extracted from biomass contains no excess of carbon than that in the biomass. Thus Green House Gas (CO_2) produced from burning of bio-fuel adds no additional CO_2 to the atmosphere like that of fossil fuels. This becomes the basic advantages of bio-fuel over the fossil fuel in maintaining the level of the Green House

Gas. Other gases like SO_x and NO_x released from the bio-oil is also less and particularly SO_x is in traces, as sulphur content in bio-oil is negligible. It has been seen that the NO_x produces is half in comparison to that of fossil fuels leading to decrease to acid rain in the atmosphere.

Conclusion:-

Bio-fuels are now being seriously viewed because of its various advantages in different fields. The depleting fossil fuels are of great concern for the future generation. More over the negative effect of fossil fuels on the environment is to be taken seriously. So bio-fuel is getting importance in the field of research and utility to take over the position of fossil fuel. It reduces the dependence of import of foreign oil and opens an alternative market opportunity for agricultural crops. Rural economy developments are also an important reason for its advantages over fossil fuel.

HTU process is cost effective route from wet biomass waste streams into diesel. The final product obtained from HDO process fully compatible with traditional transport fuels. For fuels no separate distribution system is required. Fuels can be used in existing engines. The HTU route open perspective for production of green chemicals in existing chemical installation.

Environmentally it balances the Green House Gas. With very low SO_x and NO_x release has attracted many research person and environmentalists to work in this field. Hence efficient research and utility of this bio-mass for bio-fuel production is necessary to overcome the fore coming problems due to the fossil fuels.

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