

Upgrading of Pyrolysis Bio-oil: A Review

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Abstract:

The increase in the population of the planet and the rapid economic growth and, consequently, the high consumption of energy has created many environmental problems. Due to these reasons and the lack of renewability of these fossil fuels, there has been a steep trend towards the production of renewable fuels, one of which is the production of energy from biomass. In this study, biofuel production from biomass has been investigated using the pyrolysis method, a method that reduces the production of oil from millions of years to a few seconds, and is the most industrialized thermochemical method for producing fuel from biomass. This research focuses on thermochemical processes, pyrolysis principles, hydrothermal methods and specifications, chemical composition and applications of biofuels, and the devices and equipment needed for it. It is found from this study that producing of biofuel from biomass with pyrolysis process has to solve some problems such as size of pyrolysis plant and type of feedstock. These studies suggested more economical study for producing of biofuel from pyrolysis process and also mix feedstock to increasing production quality and test some new catalyst for upgrading of biofuel.

Keywords: Biofuel, Biomass, Pyrolysis, Upgrading, Catalyst.

Introduction:

The increasing consumption of fossil fuels, despite the rapid economic growth of various societies, has led the world to a drastic change due to the emission of pollutants and its consequences. On the other hand, the limitation of fossil resources and their non-renewable resources are among the issues that have reduced the trend towards the use of fossil fuels in recent years and have led to a shift towards clean fossil fuels and renewable energy sources as a substitute for fossil fuels. One of the main options is the use of biomass energy resources. The biomass source has many advantages in comparison along with other renewable sources because of the diversification of biomass resources, different processing processes and the variety of the uses of products (Mata et al. 2010). One of the most important options for exploiting biomass resources is the production of biofuels. In general, biofuels are classified into three different generations based on the type of resources. Biodiesel is known as the first generation derived from ornamental plant sources,

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agricultural products containing sugar or starch and oilseeds or oily residues. These fuels are generally bio-ethanol, biodiesel and biogas. Second generation biofuels are referred to those biofuels derived from non-edible plant sources, cellulosic and lignocellulosic materials (Lardon et al. 2009). These fuels include biohazard, ethanol, methanol, hydrogen, dimethyl ether and synthesized diesel. The cultivation of algae for the production of biodiesel is also in the research and development stages, which is known as the source of biofuels production of the third generation. Then, biobutanol and biopropanol production in the future, these two will be categorised as biofuels for the third generation (Chisti, 2007; Mata et al. 2010). Micro-algae are a light-cellular plant that, by doing photosynthesis, converts carbon dioxide into biofuels and other valuable compounds. There are various processes for converting biomass to biofuels, which are divided into two general categories of physical processes and chemical processes. Here the chemical processes are investigated. These processes are the basis for setting up bio-refineries.

Chemical processes

Chemical processes are the most important step in converting biomass to biofuels. Generally, biomass conversion processes can be divided into two main categories, first thermochemical and the second one is biochemical processes (Fernando et al. 2006). Here is a look at thermochemical methods. Pyrolysis, gasification and liquefaction, which is carried out at thermochemical processes a several hundred degrees Celsius temperature. The diagrams of these methods are presented in the second generation sources and products.

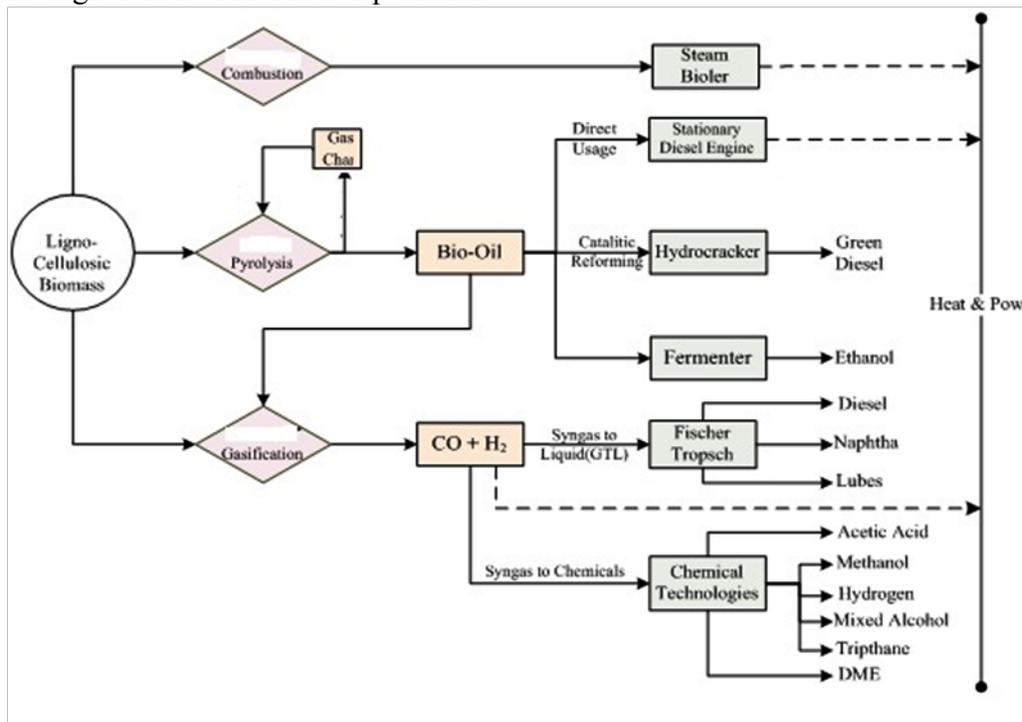


Figure 1. Different technologies for the conversion of cellulosic material (Kan et al. 2016)

Biodiesel is produced from two processes called pyrolysis and hydrothermal liquefaction from two primary sources of lignocellulose and algae, which we are discussing here these two processes, and because of the commercially implemented pyrolysis method, a more general consideration of the aspects, we will process this process.

Hydrothermal liquefaction

Hydrothermal liquefaction of near-(sub-critical) or upper (supercritical) biomass is the critical point of water (374 C, 22.1 Mpa). Density and constant dielectric, the aqueous medium plays an essential role in the solubility of organic compounds in the above and sub-critical water. The dielectric constant of water near the critical point is significantly reduced and the solubility of the organic compounds increases. The use of the following water and supercritical (hydrothermal) environment for liquefying biomass is one of the most promising technologies for the production of hydrocarbon carbohydrate (biodiesel) which is derived from direct biomass liquidation. Water acts both as a solvent and as a reactive agent. Water acts as a reactor in favor of hydrolysis reactions more than thermal decomposition and rapid decomposition of the polymer structure of polymer compounds into water-soluble products. The hydrothermal method is preferable to pyrolysis due to the production of petroleum products at the right rate. Again, the method doesn't require the drying of biomass and the biomass used that saves the cost of watering and the advantage of using biomass with different moisture content for fuel production (Chen et al. 2009).

Pyrolysis

The pyrolysis processes are carried out in atmospheric pressure and at a temperature of about 300 to 600 ° C at the absence of oxygen. The main product of the slow pyrolysis process is Charcoal, which is an old process in which the biomass is gently warmed at ranging from 300 to 400 ° C. On the other hand, rapid pyrolysis involves a large amount of heat at around 500 degrees Celsius and is associated with the fast condensation of produced vapors. This process produces highest amount of dark liquid fluid with a heat value (HV) higher than the HV of wood and about half the HV of fossil fuels. Compared to the original biomass, biofuels have many advantages: lower transport price, smaller storage tanks, and reactors transfer simplicity. A remarkable aspect in this section is that the pyrolysis process can link the agricultural industry and petrochemical processes. For more explanation, in many ways, biological processes can be integrated to fast pyrolysis by using dedicated biological refineries (for example, conversion of lignin-to-fuel residues, rapid fermentation of pyrolysis, etc.). Here, the principles of the theory of biofuel production of fast pyrolysis and the characteristics of biofuel production and possible applications of the product, equipment and method will be discussed (Li et al. 2019).

Principles of Pyrolysis

The thermal breaking down of the biomass leads to the production of unrestricted charcoal and gas and vaporous condensation (1390). This process involves the rapid transfer of heat radiation to the biomass particle and, consequently, the infiltration of heat into the particle through conduction. Under the conditions of rapid pyrolysis, the increase particle inside temperature and the kinetic energy of the corresponding internal reaction affects the rate of degradation and distribution of the product. Basically, the biomass is break down into a mixture of cellulose (hemicellulose), lignin, and a series of extracts. The purpose of the "fast" pyrolysis process is, on one hand, to hinder the breakdown of crude or catalytic material (during the formation of coal) into small condensed gas molecules, and, on the other hand, of forming and re-polymerization of coal. Such conditions, which can cause a high amount of vapor deposition, include the fast heating of biomass fragment. It is necessary to consider the timing of the initial products, both in the particle that is being decomposed and in the pre-condenser equipment. Those who first performed this process

considered the phrase "pyrolysis of flash" or "instantaneous" for a process in which small fragments (less than 1 mm) were used to obtain fuel products. The latest research (Kersten et al. 2005; Wang et al. 2005) showed that the fuel product was less dependent on the size of the biomass particles and the heater time than it was basically usually to be. Still, yet fuel production is still susceptible to these parameters. Rapidly mixing the cold flow of biomass particles with an excessive heat (eg, hot sand) cause high heat transfer to biomass particles. Several reactor designs have been discovered that may be able to achieve high thermal transfer rates, including fluid substrates and mechanical mixing devices. Moreover, to achieve a sufficient heat transfer through biomass particles, the small relative thermal infiltration depth is required that can restrict the size of the biomass particles to less than 0.2 cm (Kersten et al. 2005). The particle size here represents the real depth of particle infiltration (heat). The biodiesel produced from the raw material used in laboratory reactors and continuously operating probes is typically 60 to 70% by weight of inert dry materials. Although, as is commonly reported in the research, achieving a yield of 70% is exceptional and is limited to well-known raw materials such as cellulose. If the purpose of extracting chemicals is from biofuels, this process should be carried out in order to maximize the achievement of the desired compounds under appropriate conditions (residence time, temperature, sort of raw materials, and pre-refining of raw materials). Until recently, researchers in the field of rapid pyrolysis focused on maximizing the number of biofuels, rather than the composition and quality of the product.

Biomass composition has different behaviors at high temperature depending on the heating rates and the presence of impurity (Kersten et al. 2005). The biomass pyrolysis can be thermosetting (heat) depending on the feed and reaction temperature. The pyrolysis of holocellulose materials at temperatures below 450 °C is thermosetting and at a higher temperature, it is thermally heated. Bottles that have been decomposed within the pores of the biomass particles need more breakdowns, leading to additional gas formation, or the beads are fixed. In particular, sugar can be readily polymerized and increase the overall production of coal. This may be desirable for gentle pyrolysis, but it should be kept away in rapid pyrolysis. For small particles that are used in fast pyrolysis, secondary decomposition in particles is relatively important owing to the lack of time. But if vapors produced into the gas phase enter the environment, they will continue to decompose if condensation is not fast enough. The mechanism by which the biomass is converted into a biofuel thermal decomposition is not completely understood. Biomass consists of sugars (cellulose and hemicellulose) and polymers with a base of phenol (lignin). Due to the heat that is adequately quick, the biomass particle decomposes first into charcoal (10-15 wt%) and pyrolysis gases, which has stable vapors (CH₄, CO₂, CO) and dense fluids. Apart from all organic matter, the condensed section of pyrolysis gases also contains biomass moisture generated during breaking down. These long organic molecules (with a MW of more than about 20,000) contained in the steam are subject to a secondary thermal breakdown that might be increased by direct contact with pyrolysis coal. The fine particles of coal are easily transferred from the pyrolysis reactor and are transferred to the condenser by steam flow and accumulate along with biofuel. At the time of storage of biofuels condensed over a long period of time, the polymerization reaction can occur again, often associated with water production and possibly CO₂ emissions (Di Blasi, 2008; Mursa and Mihai, 2019; Sharma et al. 2015) .

Biofuel Specifications

As shown in Fig. 5, biofuel is a liquid in a dark brownish-red to nearly black color, depending on the chemical composition and coal content in the liquid (Hart et al. 2019).



Figure 2. Fuel derived from fast pyrolysis (Jahirul et al. 2012)

The density of this fuel is around 1200 kg / m^3 , which is considerably higher than the density of black oil. This fluid has an acidic odor that annoying the vapors of the eye. The viscosity of the fuel varies from 25 to more than 1000 cp, depending on the amount of water and the number of light components in the fuel. It should be noted that fuel specifications may change during its storage period. If the fuel contains a lot of oxygen-containing components, it is a polar nature and is not easily mixed with hydrocarbons. Normally, this fuel contains less nitrogen than petroleum products and mostly has no metal and sulfur compliments. Moreover, the nitrogen found in biomass can appear in biofuels (Van Ree and Annevelink, 2007). The products of the destruction of the components of the biomass are carboxylic acids, which cause the pH to be in the range of 2-4. This fuel is damaged by soft steel, so the fuel should be stored in acid-resistant materials such as stainless steel or polyolefin.

Water content of biodiesel is in the range of 15 - 35 wt%, which shows a significant weakness for many of its possible uses. For instance, this amount of water reduces the higher thermal value (HHV) of the biofuels by less than 19 MJ / Kg , if the thermal value of the fuel is $42\text{-}44 \text{ MJ / Kg}$, and this will apply it as a replacement for limited fuel. If the biomass does not dry below 10wt% prior to pyrolysis, the amount of water can be in the range of 30-45 wt%, which can lead to the separation of the fuel phase itself. Water in biofuels cannot be cleared by old systems such as distillation, because the heated fuel tends to be polymerized. In this way, precise control of the amount of biofuel moisture before pyrolysis is important to ensure the high quality of biofuels. The quantity of biofuel water again has beneficial effects. This quantity reduces the viscosity of the fuel that also Transport facilitation and atomic bombardment. The flame temperature is reduced in combustion that results in fewer emissions of NO_x (A Oasmaa and Kuoppala, 2003).

Chemical composition of biofuel

Hundreds of compounds are identified in the gas chromatography analysis as parts of lignin (including phenols, eugenol, guaikol) and hollow cells. Large quantities of acetic acid, stoic, and hydroxy starches are also detected. Up to now, about 50-40% of the properties of fuel components (except water) have been revealed, but large molecules, less broken or de-polymerized (due to cellulose and lignin), are not detected in fuels. The carbohydrate derivatives used in the chemical industry are some different kinds of anhydrous sugars, oligosaccharides, formaldehyde, low sulfurous alcohols and hydroxystealdehyde. According to the principles of GC analysis, in which only the distilled components in the fuel can be measured. However, many uncertain biofuel components reported in various tests (more than 30 wt% of fuel) are probably sucrose that cannot

be found by the GC analysis method, which could be used in the past (Anja et al. 2005). Since the fuel cannot be distilled well, the decomposition and decomposition technique was developed by Osama and Kavopal (Anja Oasmaa and Meier, 2005). In this method, the fuel is analyzed in a different way and identification of its various components, including the following:

- Soluble substances in water (acids, alcohols, ethyl esters);
- Ether soluble materials (aldehydes, ketones, lignin monomers, etc.);
- Insoluble materials in ether (sugars (without water), hydroxyl, acids);
- Hexane-N-soluble materials (fatty acids, extracts, etc.);
- Soluble materials in dichloromethane (DCM) (parts of lignins with low molecular weight, extracts);
- Insoluble materials in dichloromethane (degraded lignins, pieces of high molecular weight lignin, including solids).

One of the important characteristics of biofuels is the change of its properties over time. Such instability can be seen in increasing viscosity during the storage period, basically in the separation of phases, forming CO₂ and increasing the quantity of water (Saber et al. 2016). The processes by which this instability property can be solved is negligible. The precise mechanism of this "aging" process, its cause and its subsequences for future applications, is still obscure and depends on the different characteristics of the oxygen present in the fuel (as well as the type of raw material, working conditions, primary quality, storage temperature, etc.). At the temperature of the room, the aging process of biofuels happens over several months or several years, depending on the kind and quality of the raw materials. However, at high temperatures, the polymerization reaction is significantly increased, and thus it is advisable that long-term biofuel storage should be avoided at temperatures above 50 °C. Recent studies show that recycling/polymerization of parts of the fuel in combination with the evaporation of small molecules (including CO₂ CO₂ / CO) can be an important reason for the phenomenon of aging biofuels (Aho et al. 2012). Moreover, it has also been shown that this chemical in fuels is due to an increase in the dichloromethane-unsolvable materials sector and a considerable reduction in the components of unsolvable material in ether.

Applications of Biofuels

Biodiesel, having high levels of oxygen and the presence of significant amounts of water, has a much lower fuel biofuel thermal value than fossil fuels. However, combustion experiments indicate that biofuels derived from fast pyrolysis can substitute heavy and light fuels in industrial boilers. In terms of combustion properties, this fuel is more like light fuel. In general, power generation is much more favorable than the heat production process due to its added value and its ease of distribution and retrieval. Experiments were carried out by Diesel engine companies such as Arnaud Diesel and Wartsiella Diesel in collaboration with research institutes (Frigo et al. 1998). A thorough study of this was done by Venderbosch and Van Helden (Chiaramonti et al. 2007). In spite of all these difficulties, it has also been suggested that biofuel reforms and engines can make biofuels more affordable and affordable for diesel. This allowed not only independent electricity generation units, but also a high potential for biofuels in the use of transport sectors (ships, trucks, tractors, buses) in the future. The effort to develop technology and research in collaboration with manufacturers is needed to understand and realize this application.

Gas turbines

Biogas combustion experiences in gas turbines are limited. Reforms on combustion of biofuels have been reported in several cases (Chiaramonti et al. 2007).

Material and methods:

Gasification

Biofuels may also have other applications, namely the use of it as a fuel for gasification. In the refineries, the process of gasification (after combustion) is the only end method used by cheap materials that cannot be used elsewhere in the process. With regard to the biodegradation of biomass residues, pyrolysis can play an important role as a pre-treatment method, providing transportation and the management of cheaper biomass feedstock from source to gas for periods during which biomass can never be by ship and carry on economic justification. Gaseous residues can be imported into biodiesel (Higman and Van der Burgt, 2003) and the concerns in this area are mainly pH and alkaline ash content. The actual information related to small-scale gasification of biofuels has been reported by Venderbosch and colleagues (Venderbosch et al. 2002).

Fuels used for transportation

Biodiesel can also be used as fuel for transport. Initially, it was assumed that biofuels could be burned directly in diesel engines, but some impurities make it unfit for diesel engines. In this way, biofuels should be improved for good transportation. Generally, biofuels are promoted in FCC reactors under pressure from high-pressure hydrogen reactors or atmospheric pressure. Some researchers advocate the shared refinement of upgraded biofuels along with the raw fuels (Gutierrez et al. 2007). Improved biofuels have been discussed further for its use as a fuel for transportation by Vanderbosch et al. (Venderbosch et al. 2010) and Wildschut et al. (Wildschut et al. 2009).

Resins to protect chipboard or multilayer boards

Biofuel has been studied for replacing phenol-formaldehyde resins in chip production due to the high binding power of lignin derivatives in biofuels. In a 2000 study, it was concluded that biofuels can be used to produce resin instead of phenol at 50% (de Miguel Mercader et al. 2008). Another advantage is that the products of lignin analysis and their products are suitable for soil conditions, soil acidity control, improving the effects of aluminium and excess iron, increasing the availability of phosphates and increasing products. In addition, these compounds are very good complex agents for nutrients (Venderbosch et al. 2010).

Biodiesel components

In bio-derived wood, there are some significant oxidative compounds available in significant amounts. Such recovery of pure biofuel compounds may be technically practicle but is not economically possible due to the high expenses of recovering chemicals and their low condensation in fuel. Below are the relevant chemical components.

Wood spices

Liquid smoke is the commercial use of biofuels derived from wood. It produces a red solution that may be sprayed before baking meat. So the taste, color, and smell of meat are “synthetic”. The range of food flavoring products, depending on biofuels, has been traded by Red Covers (USA)

and Chamviron (Germany). One of the patents is presented here as an example (Wildschut et al. 2009).

Phenolic compounds

The lignin component derived from biofuels consists of phenol, eugenol, crossoul, xylene, and more amounts of alkali (poly) alkaloids (called so-called insoluble pyrolytic lignin in water). Recovery of phenolic compounds has been reported to be over 50 wt%, but this amount is only derived from certain raw materials. The values of smaller phenolic compounds, which are more expensive, are limited in biofuels, either, because that the lignin-derived monomers in the pyrolysis medium have a very high reactivity or the primary lignin present in the biomass is only partially depolymerized (Wildschut et al. 2009).

Pyrolysis equipment

Production of charcoal is the goal of slow pyrolysis, while rapid pyrolysis is done with the aim of converting the biomass to the maximum amount of liquid. When a biofuel product is used to capture the fuels or chemicals required for transportation, factors other than the duration of the vapor should be taken into consideration. The fuel composition may be managed by process circumstances, equipment size, and the type of catalysts (Wright et al. 2010).

Input flow to the reactor

Initial measures for rapid pyrolysis were implemented in flow reactors in which biomass size (1-5 mm) were introduced into a warm and still gas stream. It was assumed that the reaction lasted for a few seconds at a time, provided that the reactor tube was maintained at 700-800 ° C.

Reducing reactor

Reduced pyrolysis was considered as another method for flow injection reactors. The surface heated by the hot gas stream begins to rotate when the biomass is compressed (at around 600 °C). The gas flow from pyrolysis or coal gas is generated. Generally, the reluctant pyrolysis has two main flaws. Its first disadvantage is the problem of achieving an adequate amount of heat from hot gases to a dampening level. The second is its limitation, the difficulty of making contact with raw materials in various forms (shape, structure, and density of particles) with a decreasing level. In practice, the raw material is relatively small in proportion to the reduction of pyrolysis.

The turbulent fluid bed

The turbulent fluid bedding method is one of the best methods of fast heating to biomass particles. In this pyrolysis, the gas is injected vertically from bottom to top through a fine sand material substrate with sufficient viscosity to create a strong mix of gas and solids in an emulsion that is similar to a fluid. Liquid substrates are described by transferring heat and mass between gas and particles and submerged material. This condition is very convenient for fast pyrolysis because the biomass is quickly heated and the released gases are rapidly transmitted from the reactor. This bed is heated by external combustion or coal produced and heated by direct heat transfer or indirect heat Transmits While the transfer of heat from sand to the biomass may be very favorable and

excellent, heat transfer from the heat sink to the fluid bed due to the internal thermal resistance of the coil and the propulsion force will be limited to about 300 °C.

The wide scale of the pyrolysis of the fluid bed is limited due to the limitation in the amount of heat that can be transmitted through submerged pipes in fluid substrates. In direct-heat-transfer from the twin-fluid substrates, the second bed where pyrolysis occurs is also used to transfer solids that are heated by burning of coal gas in a bed (Brown and Holmgren, 2009).

Circulating fluid bed

Circulating fluid bed (CFBs) differs from the amount of gas used to fluidize the bed with a turbulent fluid bed. In the circulating surfaces, this flow of gas is deliberately raised so that the particles are transferred out of the bed, then retrieved by cyclones and opened to the fluid bed. It provides direct transfer of heat to a fluid medium; the design and operation of this system are more complicated than the reactor with turbulent fluid bedding.

CFB technology, despite the turbulent fluid bedding, is relatively advanced, but there are also problems. The challenge of quick pyrolysis is to clean enough of the incompressible gases from rapid pyrolysis to re-heat and compress. Finally, in order to realize the high maintenance of relatively light solids in upstream systems in solids flow rates of 10-20 g / cm²s, the gas flow rate in the rising section should be high and about 1000m³ / h (biomass tons / h) (Choi, 1977).

Moving-grate Vacuum Pyrolysis

This process involves a combination of quiet and rapid pyrolysis conditions. Hard solids are heated relatively slowly to temperatures exceeding the warm pyrolysis temperature, while at high temperatures, the gas is nearly eliminated rapidly by using a process pressure drop of 0.02-0.2 bar. An effort was made to commercialize this process in the late 1990s by Pyrovac International. Biomass is indirectly transferred to a horizontal iron network through a mixture of molten salts combined with KNO₃ and NaNO₃. The salt is heated by an incombustible gas emitted from the pyrolysis process. The limitation of heat transfer requires that the particles of the substrate become turbulent, but the obvious limitations of internal heat transfer cannot be avoided.

Result and discussion

Improving the quality of biofuels

The biofuels feature can be enhanced in several methods: through physical, chemical and catalytic.

Biochemical and catalytic enhancement

Biofuels can be promoted in several methods: chemically, physically and catalytically. This issue has been thoroughly investigated and only the recent advances have been reported here (Diebold and Bridgwater, 1997).

Biofuel Fuels Upgrade

The most important features that may have an adverse effect on the quality of biofuels are the incompatibility with older fuels due to the high oxygen content of biofuels, high amounts of solids, high viscosity and chemical instability.

Filtration

Hot steam filtration may decrease the amount of fuel ash to less than 0.01%. This increases the quality of the product with a low amount of charcoal.

Adding Solvent

For homogenize and reduce the viscosity of biofuels, Polar solvents have been used for many years. Adding solvents, particularly CH₄OH, had a notable impact on stability of fuel (Zhang et al. 2007).

Emulsions

The pyrolysis fuels do not interfere with fossil fuels but can be emulsions with surfactants with diesel fuel (Bridgwater, 2012).

Biofuel Catalytic Upgrade

Natural ash in biomass

Prior to considering catalytic biofuel upgrades, it is important to understand at first that biomass contains highly catalysts in itself. These catalysts are alkaline metals from ash and essential for the transfer of nutrients and the growth of biomass. The most active alkali metal is K and then Na. These catalysts break down the secondary vapors, reduce the fluid yield and reduce its quality. The researchers' efforts to remove ash are available.

Upgrading biofuels

The promotion of biofuels for the conversion of fuels, which are usually suitable for transportation, requires complete distillation and refinement, which can be realized with pyrolysis integrated with a catalyst or by a separate operation. A minor upgrade to a product that is compatible with the refinery's flows is also being considered in order to take advantage of the economic benefits and refinery experiences. Integration with the refinery has been investigated by upgrading fuel through cracking or water purification (Zhang et al. 2007):

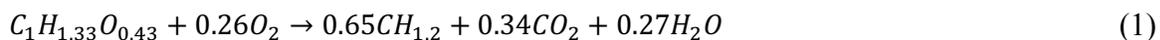
- Water purification
- Catalytic steam cracker
- Esterification
- Gasification to generate combined gas and the synthesis to produce alcohols or hydrocarbons

Water purification

Hydroprocessing, by a catalytic reaction with hydrogen, disperses oxygen into the water. This process is regarded as a preferable process for quick pyrolysis. This process usually occurs at high pressures and medium temperatures and requires a hydrogen source (Hosseinpour et al. 2017).

Cracking zeolite

The cracking of zeolite releases oxygen as carbon dioxide, which is shown in the form of the following chemical formula:



The upgrade through zeolite can be done along the pyrolysis process, or it can be regenerated to enhance liquids or fluids (Ardiyanti et al. 2009). The report of Hydrocarbon Publications on Future Catalytic Fluid Cracking (FCC) and hydrogen processing in new refineries suggests that biomass-derived fuels can best be promoted by HZSM-5 or ZSM-5 since these catalysts Zeolite increases the efficiency of liquid and propylene products (Vitolo et al. 1999). Unfortunately, these input materials tend to be flooded, and TANs (high total number of acids) and adverse products such as water and carbon dioxide are among the other challenges. There is a great concern in developing the quality of biofuels, and a number of these improvements have integrated the catalytic decomposition with the Pyrolysis over the past few years. These hybrid pyrolysis-catalytic decomposition reaction systems have been studied by a number of organizations and have incorporated numerous business advances. Other actions in the field of pyrolysis combined with catalytic decomposition were carried out by a number of laboratories, which resulted in little success. A common problem is an aim of improving the quality of biofuels without defining its purpose and specifying the characteristics examined. The combination and integration of catalytic decomposition and pyrolysis need a unique temperature and a catalyst with sufficient strength to withstand temperature and mechanical conditions. In this way, there is little flexibility in working conditions, indicating that catalyst systems are complex. As coking is an issue and the mechanism by which oxygen is removed from biofuels, catalyst reprocessing is an important phase in reactor design.

Steam up close-coupled. Steam catalytic cracking using acidic zeolite catalysts leads to deacidification, which results from the synergistic dehydration-de-carboxylation which is associated with the production of mainly aromatics at 450 °C at atmospheric pressure. Eventually, oxygen is released as CO₂ and CO from the secondary oxidation reactor for coke combustion deposits under the catalyst. This is done more by the FCC at the refinery. The low proportion of H / C in biofuels results in relatively limited hydrocarbon constraints. Appropriate aromatics from the biomass to blend with gasoline are 20% by weight and 45% energy. The aromatic crude product can be sent to the refinery for refining. Some recent actions in the NREL have been carried out in a close-coupled reactor. Although the problem of coking with zeolite can essentially be conquered by the FCC, along with the repeated production and catalyticization of the coke oxidation. Concerns about the weak control of size and shape with conventional zeolites and tendency to form toxic gases. the process cost is high and the products are not competing with fossil fuels (Mahfud et al. 2007).

Other methods for promoting the chemical composition of biofuels

Non-physical ways and those catalytic processes that are not covered by hydration processes and associated with zeolite, is presented in this section (Chang, 2008; Zhang et al. 2006) .

Water phase processing

This is a moderately new method initially suggested by Dumesic et al., Which provided aqueous solutions of hydrocarbon oxides through the reformation of hydrophobic and hydrogen dehydrogenation, hydrogen and alkanes (Peng et al. 2008; van Rossum et al. 2009). A large proportion of biofuels are water-soluble and the compounds in the aqueous solution are greatly oxygen-enriched hydrocarbons. It indicates that the hydrophilic process can be used to produce hydrogen and alkanes from the biofuel sector.

Gentle Cracking

Another method for cracking based on zeolite is a gentle cracking using base catalysts, which only covers cellulose and hemicellulose-derived products, and aims to reduce carbon footprint and gas formation (Tang et al. 2008).

Steam Reforming

The soluble part in biofuel (carbohydrate derivatives) can be converted to steam by steam reforming. This process was carried out in a fluidized bed process using commercial catalysts and nickel under a temperature same that of natural gas reclamation. This process depends on the use of durable aqueous derivative derived from biofilm lignin; for example, the use of phenol as an alternative to phenol-formaldehyde resins by upgrading these organic components (Rioche et al. 2005).

Conclusion

The rapid pyrolysis makes possible the rapid and inexpensive breakdown of the molecular polymer molecules. Business procedures have been expanded by a number of companies, such as BTG (Netherlands), Dynamo (Canada) and Ensin (the USA and Canada). Although fuel and valuable chemicals are long-term biofuels, there are other more important goals, including heat and electricity production. Advances in the analysis of biofuels and the promotion of biofuels should be taken into account for various applications. Despite nearly 30 years of experience in the production and operation of biofuels, analyzes are mostly imperfect or unable to be repeated in other laboratories. Nowadays, they realize that the GC analysis does not provide a perfect image of the biofuels compound. Improving biofuels not only needs a more comprehensive realization of the principles of chemoprophylaxis but also requires an understanding of the biofuels' chemical chemistry. An important issue that needs to be noted is the precise function of oxygen-based operating groups in fuel and determining which one is preferable. Considering the limited status of fossil fuels and finding a method for producing alternative oil from the present, biofuel production of fast and hydrothermal pyrolysis is recommended as a convenient and economical approach, which is the start of the launch of biofuel refineries. This method still has many unresolved problems that are gradually going to be solved by the researchers, and the possibility of large-scale economic production is under investigation and consideration. It is found from this study that producing of biofuel from biomass with pyrolysis process has to solve some problems such as size of pyrolysis plant and type of feedstock. These studies suggested more economical study for producing of biofuel from pyrolysis process and also mix feedstock to increasing production quality and test some new catalyst for upgrading of biofuel. There are several techniques for bio-oil upgrading. Each method has its own advantages and disadvantages. Solvent addition and emulsification are physical operations and seem to be short-term approaches for bio-oil upgrading. Among chemical operations, most methods require high temperature and/or high-pressure processes which result in high cost of upgrading. Esterification can be done at atmospheric pressure and low temperature, but it has no considerable effect for denitrogenation. Hydrotreating seems to be a promising approach since it has been used in oil refineries for many years and the process is well established, but more efforts are needed to resolve the problem of coking and catalyst deactivation. Upgrading of bio-oil has drawn attention from researchers around the world, but a

little work has been published on upgrading of algal bio-oil which opens a new route for future research work. There is not any comprehensive research on economic evaluation of all upgrading techniques for algal bio-oil. Therefore, it is not possible to determine the most economical method for bio-oil upgrading at the present time. Hence, economic evaluation and scale-up could be one of the interesting topics for future research.

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