Review of First and Second Generation Bio-fuels – Production & Use as alternate fuels in CI Engines

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ABSTRACT: **A sustainable resource of energy contributes in growth of sustainable economic and industrial fields. The 'first-generation' bio-fuels appear unsustainable because of the potential stress that their production places on food commodities. For organic chemicals and materials these needs to follow a bio refinery model under environmentally sustainable conditions. Where these operate at present, their product range is largely limited to simple materials (i.e. cellulose, ethanol, and bio-fuels). Second generation bio refineries need to build on the need for sustainable chemical products through modern and proven green chemical technologies such as bio processing including pyrolysis, Fisher Tropsch, and other catalytic processes in order to make more complex molecules and materials on which a future sustainable society will be based. This review focus on cost effective technologies and the processes to convert biomass into useful liquid biofuels and bio products, with particular focus on some bio refinery concepts based on different feedstock's aiming at the integral utilization of these feedstock's for the production of value added chemicals.**

Keywords: Bio-fuels, Esterification, Feedstock, Bio-products

INTRODUCTION

Major research emphasis was given for the development of petroleum, coal, and natural gas based refinery to exploit the cheaply available fossil feed stock in the twentieth century. This feedstock are used in industry to produce multiple products such as fuel, fine chemicals, pharmaceuticals, detergents, synthetic fiber, plastics, pesticides, fertilizers, lubricants, solvent, waxes, coke, asphalt, etc. to meet the growing demand of the population [Demirbas MF, 2006, Haung HJ, 2008]. The fossil resources are not considered as sustainable and questionable from the economic, ecology and environmental point of views [Osamu K, et al, 1989]. The use of fossil fuels is a big parameter for increasing the level of CO_2 in the atmosphere which is directly associated with global warming observed in recent decades [Stevens CV, 2004]. The adverse effects of greenhouse gas (GHG) emissions on the environment, together with declining petroleum reserves, have to be taken seriously. Therefore, the quest for sustainable and environmentally benign sources of energy for our industrial economies and consumer societies has become urgent in recent years [Gomez LD, et al, 2008]. Consequently, there is renewed interest in the production and use of fuels from plants or organic waste.

New income and employment opportunities in rural areas may be created by bio-fuel production along with bio products. Current century is hoping for a shift to alternate industrial feedstock and green processes to produce these chemicals from renewable biomass resources [Fernando S, 2006]. We get some CO_2 benefits and improved domestic energy security by use of 'First generation' bio-fuels. But major difficulty is about the sourcing of feedstocks. A 'first generation' bio-fuel (i.e. biodiesel (bio-esters), bio-ethanol, and biogas) is characterized both by its ability to be blended with petroleum-based fuels, burning in existing internal combustion engines, and distributed through existing infrastructure. The production of 1st generation bio-fuels is commercial today, with almost more than 90 billion liters produced annually.

The main disadvantage of first generation bio-fuels is the food-versus-fuel debate, one of the reasons for rising food prices is due to the increase in the production of these fuels [Gomez LD, et al, 2008]. Additionally it is claimed that biodiesel is not a cost efficient emission abatement technology. Therefore due to many advantages and disadvantages of the 1st generation bio-fuels and obvious advantages of 2nd generation bio-fuels as shown in Fig. 1, the approaches to integral utilization of biomass for sustainable development are more reasonable, where all parts of the plant such as leaves, bark, fruits, and seeds can be utilized to useful products. The term 'Bio refinery' was initially established by NREL during 1990, for the utilization of biomass for production of fuels and other bio products. This term refers to a facility (or group of facilities) which combines the production of materials, chemicals, or fuel products with energy production.

The bio refinery system includes biomass production, biomass transformation/processing, and end use. The total biomass production on earth is approximately 110 billion tones organic dry matter of land biomass per annum and 55 billion tons of aquatic biomass. The part of it is used as food, feed, energy and industrial raw materials, where food use is only 1.5% of the entire land biomass. The rest of the biomass is unused or recycled in to the earth system, which can be used as raw material for chemical production. Currently, starches, sugar, oils and fats, cellulose, rubbers have been used industrially as well [Fernando S, 2006]. So far many research papers on the bio refinery concept have been published: wheat straw bio refinery, corn bio refinery and forest residue based bio refinery [Gomez LD, et al, 2008], etc.

Brief about biodiesel

Bio-fuels were used as primary fuel long back. Bio-fuels and bio-energy are as old as civilization itself. Solid bio-fuels like wood, dung and charcoal have been used ever since man discovered fire, and are still used today for cooking and heating in many communities in developing countries. Even liquid bio-fuels such as olive oil and whale oil have been used as fuel.

After 1900, wood fuels were largely replaced by fossil fuels. This also helped reduce unsustainable use of timber resources at the time, which had drastically increased in price during the century.

Bio-fuels were our first transportation fuels The first cars ever built were made to function on bio-fuels, rather than fossil fuels:

- The first internal combustion engine to be patented in the US in 1826 was designed to run on a blend of ethanol and turpentine (derived from pine trees).
- Henry Ford designed his original 1908 Model T to run on ethanol
- Rudolph Diesel intended to power his engine with vegetable oil

The emergence of large-scale petroleum Fossil fuels have also been used since ancient times in various forms on a small scale. However, it was in the mid-1800s that they began to be commercialized and available on a large scale. At this time, coal became widely available; kerosene, the first combustible hydrocarbon liquid, was invented; and drilling of the first commercial oil wells began. Consequently, the large supply, the low price, the efficiency and practicality of fossil fuels reduced our appetite for bio-fuels at this time. Also, the prohibition movement in the U.S. stopped bio-fuels development in its tracks, while it was still in its infancy, and encouraged use of fossil fuels.

Come back of bio-fuel in use

During World War I, there were (fossil) oil shortages, and therefore ethanol was in high demand, as it became known that ethanol could be blended with gasoline for a suitable motor fuel. More recently, there have been several (fossil) oil crises since the 1970s that prompted renewed interest in biofuels:

- 1973 oil crisis: caused by the Organization of Arab Petroleum Exporting Countries (OAPEC) oil export embargo.
- 1979 oil crisis: caused by the Iranian Revolution.
- 1990 oil price shock: caused by the Gulf War.

This led many countries, such as the US and Brazil to begin modern large-scale production of biofuels. In the last 10 years, biofuels have been embraced as a way to help resolve some of the world's greatest challenges: declining fossil fuel supplies, high oil prices and climate change. And that is the story of how biofuels came to be, why they were largely forgotten and how they were recently rediscovered with renewed interest.

Advantages of biodiesel fuel

1) It is a renewable energy source.
2) It is less polluting than other fuels.
3) The life of catalytic converters is improved because of lack of sulfur.
4) It can also be blended easily with other energy resources and oil.
5) It can be used in existing diesel engines without any alterations.
6) It can also be distributed through existing diesel fuel pumps, which is another biodiesel fuel advantage over other alternative fuels.
7) The lubricating property of the biodiesel may lengthen the lifetime of engines.

Disadvantages of biodiesel fuel

1) At present, Biodiesel fuel is one and a half times more expensive than petroleum diesel fuel.
2) It requires energy to produce biodiesel fuel from soy crops, plus there is the energy of sowing, fertilizing and harvesting.
3) Another biodiesel fuel disadvantage is that it can harm rubber hoses in some engines.
4) As Biodiesel cleans the dirt from the engine, this dirt can then get collected in the fuel filter, thus clogging it. So, filters have to be changed after the first several hours of biodiesel use.
5) Biodiesel fuel distribution infrastructure needs improvement, which is another of the biodiesel fuel disadvantages.

First generation biodiesel

The first generation bio-fuels are those fuels that have been derived from sources like starch, sugar, animal fats and vegetable oil. The oil is obtained using the conventional techniques of production. Some of the most popular types of first generation bio-fuels are:

Biodiesel: It is the most common type of bio-fuel commonly used at present. Ttransesterification is the process for producing bio-diesels. This fuel if very similar to the mineral diesel and is chemically known as fatty acid methyl. This oil is produced after mixing the biomass with methanol and sodium hydroxide. The chemical reaction thereof produces biodiesel. Biodiesel is very commonly used for the various diesel engines after mixing up with mineral diesel. Now in many countries the manufacturers of the diesel engine ensure that the engine works well even with the biodiesel.

Vegetable oil: These oils can be either used for cooking purpose or even as fuel. The main fact that determines the usage of this oil is the quality. The oil with good quality is generally used for cooking purpose. Vegetable oil can even be used in most of the old diesel engines, but only in warm atmosphere. In most of the countries, vegetable oil is mainly used for the production of biodiesel.

Biogas: Biogas is mainly produced after the anaerobic digestion of the organic materials. Biogas can also be produced with the biodegradation of waste materials which are fed into anaerobic digesters which yields biogas. The residue or the by product can be easily used as manure or fertilizers for agricultural use. The biogas produced is very rich in methane which can be easily recovered through the use of mechanical biological treatment systems. A less clean form of biogas is the landfill gas which is produced by the use of naturally occurring anaerobic digesters, but the main threat is that these gases can be a severe threat if escapes into the atmosphere.

Bio alcohols: These are alcohols produced by the use if enzymes and microorganisms through the process of fermentation of starches and sugar. Ethanol is the most common type of bio alcohol whereas butane and propanol are some of the lesser known ones. Biobutanol is sometimes also referred to as a direct replacement of gasoline because it can be directly used in the various gasoline engines. Butanol is produced using the process of fermentation, and some of the experiments have also proved that butanol is a more energy efficient fuel and can be directly used in the various gasoline engines.
Syngas: This gas is produced after the combined process of gasification, combustion and pyrolysis. Bio-fuel used in this process is converted into carbon monoxide and then into energy by pyrolysis. During the process, very little oxygen is supplied to keep combustion under control. In the last step known as gasification the organic materials are converted into gases like carbon monoxide and hydrogen. The resulting gas Syngas can be used for various purposes.

Second generation of biodiesel
Second generation bio-fuels are also known as advanced bio-fuels. The feedstock used in producing second generation bio-fuels are generally not food crops is the major difference from first generation bio-fuels. The only time the food crops can act as second generation bio-fuels is if they have already fulfilled their food purpose. For instance, waste vegetable oil is a second generation bio-fuels because it has already been used and is no longer fit for human consumption. Virgin vegetable oil, however, would be a first generation bio-fuel.
Because second generation bio-fuels are derived from different feed stock, Different technology is often used to extract energy from them. This does not mean that second generation bio-fuels cannot be burned directly as the biomass. In fact, several second generation bio-fuels, like Switch grass, are cultivated specifically to act as direct biomass.

Second Generation Extraction Technology
For the most part, second generation feedstock are processed differently than first generation biofuels. This is particularly true of lignocellulose feedstock, which tends to require several processing steps prior to being fermented (a first generation technology) into ethanol. An outline of second generation processing technologies follows.
Thermochemical Conversion*:* The first thermochemical route is known as gasification. Gasification is not a new technology and has been used extensively on conventional fossil fuels for a number of years. Second generation gasification technologies have been slightly altered to accommodate the differences in biomass stock. Through gasification, carbon-based materials are converted to carbon monoxide, hydrogen, and carbon dioxide. This process is different from combustion in that oxygen is limited. The gas that result is referred to as synthesis gas or syngas. Syngas is then used to produce energy or heat. Wood, black liquor, brown liquor, and other feedstock are used in this process.
The second thermochemical route is known as pyrolysis. Pyrolysis also has a long history of use with fossil fuels. Pyrolysis is carried out in the absence of oxygen and often in the presence of an inert gas like halogen. The fuel is generally converted into two products: tars and char. Wood and a number of other energy crops can be used as feedstock to produce bio-oil through pyrolysis.
A third thermochemical reaction, called Torre faction, is very similar to pyrolysis, but is carried out at lower temperatures. The process tends to yield better fuels for further use in gasification or combustion. Torre faction is often used to convert biomass feedstock into a form that is more easily transported and stored.
Biochemical Conversion
A number of biological and chemical processes are being adapted for the production of biofuel from second generation feedstock. Fermentation with unique or genetically modified bacteria is particularly popular for second generation feedstock like landfill gas and municipal waste.

Common Second Generation Feedstock
To qualify as a second generation feedstock, a source must not be suitable for human consumption. It is not a requirement that the feedstock be grown on non-agricultural land, but it generally goes without saying that a second generation feedstock should grow on what is known as marginal land. Marginal land is land that cannot be used for "arable" crops, meaning it cannot be used to effectively grow food. The unspoken point here is that second generation feedstock should not require a great deal of water or fertilizer to grow, a fact that has led to disappointment in several second generation crops.
Grasses: A number of grasses like Switch grass, my canthus, Indian grass, and others have alternatively been placed in the spotlight. The particular grass chosen generally depends on the location as some are more suitable to certain climates. In the United States, Switch grass is favored. In Southeast Asia, My canthus is the choice.
The advantages of grasses are:

- They are perennial and so energy for planting need only be invested once
- They are fast growing and can usually be harvested a few times per year
- They have relatively low fertilizer needs
- They grow on marginal land
- They work well as direct biomass
- They have a high net energy yield of about 540%

The disadvantages of grasses are:

- They are not suitable for producing biodiesel
- They require extensive processing to made into ethanol
- It may take several years for switch grass to reach harvest density

- The seeds are weak competitors with weeds. So, even though they grow on marginal land, the early investment in culture is substantial
- They require moist soil and do not do well in arid climates.

Water demands are the biggest drawback to grasses and the factor that keeps them from becoming more popular as second generation biofuels.

Jatropha and other seed crops: Seed crops are useful in the production of biodiesel. In the early Part of the 21st century, a plant known as Jatropha became exceedingly popular among biodiesel advocates. The plant was praised for its yield per seed, which could return values as high as 40 percent. When compared to the 15 percent oil found in soybean, Jatropha look to be a miracle crop. Adding to its allure was the misconception that I could be grown on marginal land. As it turns out, oil production drops substantially when Jatropha is grown on marginal land. Interest in Jatropha has waned considerably in recent years.

Other, similar seed crops have met with the same fate as Jatropha. Examples include Cammelina, Oil Palm, and rapeseed. In all cases, the initial benefits of the crops were quickly realized to be offset by the need to use crop land to achieve suitable yields.

Waste Vegetable Oil (WVO): WVO have been used as a fuel for more than a century. In fact, some of the earliest diesel engines ran exclusively on vegetable oil. Waste vegetable oil is considered a second generation biofuels because its utility as a food has been expended. In fact, recycling it for fuel can help to improve its overall environmental impact.

The advantages of WVO are:

- It does not threaten the food chain
- It is readily available
- It is easy to convert to biodiesel
- It can be burned directly in some diesel engines
- It is low in sulphur
- There are no associated land use changes

The disadvantages of WVO are:

- It can decrease engine life if not properly refined

WVO is probably one of the best sources of biodiesel and, as long as blending is all that is required, can meet much of the demand for biodiesel. Collecting it can be a problem though as it is distributed throughout the world in restaurants and homes.

CONCLUSION:-

The paper has discussed first and second generation bio-fuels, production methods of these bio-fuels, bio refineries, and associatet challenges. However, more concerns over first generation bio-fuels in terms of their use, production, cost comparison & environmental issues is necessary to address in future.

The unfortunate effect is that bio-fuel is starting to generate resistance particularly in poor countries with environmental agendas. However the immediate use of first generation bio-fuels involves putting in place logistic changes to use bio-fuels.

This commitment to bio-fuels in the present will make the transition to the second generation bio-fuels more economically convenient. But at present the technology to produce these replacement fuels is still being developed. Bio refineries based on lingo cellulosic will be able to access a much wider variety of feedstock, including forest biomass. Therefore, there is a need to integrate process operation, reactor and catalyst design to improve the effectiveness of different processes used for bio products and bio-fuels production in a typical bio refinery system.

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