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Bio-Oils Alternative to Petroleum Fuels

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Energy has taken a pivotal point in the activities of man, knowingly and unknowingly. Fossil fuels continue to be a critical source of energy and materials for the petrochemical industry in the medium term. However, the finite, non-renewable nature and contributions to global warming has heightened the search for sustainable alternatives (Ong and Bhatia, 2010). The increased greenhouse gas (GHG) emissions as a result of the extensive use of fossil fuels will need to be curbed before catastrophic damage is done, these greenhouse gases contribute significantly to global warming resulting in an adverse impact on the climate. Emerging from the climate deal that was struck at the Conference of Parties (COP 21), the average temperature rise was pegged at just over 1 °C, with Paris 2015 setting a 2 °C cap as the target by 2050 to limit damage to the ecosystem (Hassan *et al.*, 2015). The use of fossil fuels needs to be reconsidered in light of the pollution issues, significant uncertainties surrounding the longevity of petroleum reserves, and fluctuating crude oil prices that have a significant impact on non-oil producers and continuously impact economic development. The risk of instability in the vast majority of the areas that produce crude oil is another important worry. To make progress in overcoming the numerous obstacles and risks associated with using fossil fuels, scholars have continued to to search for viable substitutes that might act as fossil fuel alternatives fuels. Nonetheless, the preferred fuels must to be ecologically sustainable among other appealing attributes. Biofuels are derived from materials that were once living and such fuels easily find themselves being a part of photosynthesis cycle making them renewable and potential substitutes to traditional fuels. Biomass has significant potential to become more widely used as biofuel feedstock due to its numerous advantages with the resources widely distributed, abundant globally, and renewable in nature. Vegetable oils have proven to be valuable resource in the production of biofuels with both edible and non-edible oils having successful trials and implementation in the sector. Issues related to land use change, water utilisation and food vs. fuel debate continue to slow the growth of the sector as these factors are vital for the successful commercialisation of the sector on a large scale. Bio-oils are dark brown, free-flowing organic liquids that are comprised of highly oxygenated compounds. The synonyms for bio-oil include pyrolysis oils, pyrolysis liquids, bio-crude oil (BCO), wood liquids, wood oil, liquid smoke, wood distillates, pyroligneous acid, and liquid wood. Pyrolysis liquids are formed by rapidly and simultaneously depolymerizing and fragmenting cellulose, hemicellulose, and lignin with a rapid increase in temperature. Rapid quenching then "freezes in" the intermediate products of the fast degradation of hemicellulose, cellulose, and lignin. Rapid quenching traps many products that would further react (degrade, cleave, or condensate with other molecules) if the residence time at high temperature was extended. Bio-oils contain many reactive species, which contribute to unusual attributes. Chemically, biooil is a complex mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids. It also contains other major groups of compounds, including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics. Throughout this review, the terms pyrolysis oil, tar, pyrolytic tar, and bio-oil will be used. The four different generation of biofuel mentioned in below table:

Table 1. Types of biofuels generations: Their bio-masses sources and products

Biofuels 'generation	Source	Product
First generation	Starch, Sugars, Seed oils	Bioethanol, Biodiesel, Biogas
Second generation	Ligno-cellulosic Biomass or woody crops, Jatropha, Waste plant materials	Bio oil, or pyolytic oil, Syngas
Third generation	lignocellulosic biomass	Biodiesel, Unsaturated oils
Fourth generation	Specially designed engineered microorganisms and plants, Genetically modified microalgae	Carbon-negative fuels, Biohydrogen, Biomethane

Properties of Bio-oils Bio-oils are typically dark brown, free-flowing liquids, characterized by their complex mixture of organic compounds, including acids, alcohols, aldehydes, esters, ketones, phenols, and lignin-derived oligomers. Their physical and chemical properties significantly differ from those of petroleum-derived oils, primarily due to their distinct chemical composition. Key properties of bio-oils from various sources include:

		Bio-oil from Wood Pyrolysis	Bio-oil from Heavy Petroleum Fuel
Moisture content	:	15-30%	0.1%
Specific Gravity	:	1.2	0.94
Elemental Composition	:	C (54-58%), H (5.5-7.0%), O (35-40%), N (0-0.2%)	C (85%), H (11%), O (1.0%), N (0.3%)
Ash Content	:	0-0.02%	0.1%
Viscosity (at 50°C)	:	40-100 cP	180 cP
Solids	:	0.2-1.0 %	1.0%
Distillation Residue	:	Up to 50%	Up to 1.0%

Production of biomass oils

An essential first step in using plant oils in society's everyday lives is their production and extraction. There are several sources of biomass (plant) oils, including seeds, nuts, fruit, and lignocellulose material. Extraction is a crucial step in order to produce the value product. Cleaning, drying, crushing, pressing, oil recovery, and purification are some of the operations that might come before or after extraction. Depending on the kind of plant and the extraction treatment methods used, various yields and grades of oil may be produced. When oil recovery is rather challenging, solvent extraction is another method that can be used to extract oils from plant material. Once the oil is dissolved, the solvent is removed by distillation, and impurities such as water are removed, to leave pure vegetable oil. The oil extracted from plant material is useful as food, raw materials for cosmetic and drugs, however because of its potential as biofuel feed-stock this use cannot be ignored and its application in this sector has been increasing. Different techniques have been explored in the utilisation of biomass oils for the production of fuels. Plant oils such as palm, soya, sunflower, rapeseed oil have been used as feedstock in the production of 1st generation biofuels both from virgin and from used oil as the feedstock is part of the edible oil mix for human consumption. Perennial plants such as Jatropha have been explored as oil producing feedstock to support biofuel production (Prasad, 2010). The choice of feedstock production has been influenced by geographical location as well as supporting policies put in place by authorities, In South Africa for example, Jatropha plant was deemed invasive and banned from production as a biofuel feedstock. Jatropha which is perennial crop though offer advantages in the sense that it is non-edible and can be grown on marginalised land but concerns over tillage and use of mechanical equipment on land have been raised. Biomass derived oils come in different forms based on source, extraction technique and these include triglycerides based oils derived from oil bearing crops or seeds as well as pyrolytic or bio- oils obtained through the thermal degradation of biomass material in the absence of oxygen. The two type of oils mentioned above have shown potential to be useful as transportation and chemical feedstocks, however undesirable physicochemical properties makes them unsuitable for direct use. For triglycerides, which have about 9–13% oxygen content, a characteristic high viscosity as well as hydrolytic and oxidative instability based on the fatty acid profile present problems.

Processes for Conversion

Biomass can be converted to bio-oil through flash pyrolysis and hydrothermal liquefaction. Flash pyrolysis quickly decomposes organic materials, producing bio-oil, char, and gas. Hydrothermal liquefaction operates under elevated pressure and temperature, producing biocrude and various byproducts. Both processes, while simple and cost-effective, generate a range of products, including char. Research indicates that conditions such as substrate type and reaction parameters significantly influence yields. Bio-oils, derived from biomass through various processes such as pyrolysis and hydrothermal liquefaction, present a promising alternative to conventional petroleum-based fuels. They offer renewable energy solutions and serve as feed stocks for a variety of chemical products.

Cellulose → Aqueous product → Gases ($4H + CO_2 \rightarrow CH_4 + 2H_20$)

Transesterification: When a triglyceride and an alcohol molecule mix, glycerol and alkyl esters are produced as byproducts. This process is known as transesterification. Catalyst impact, which aids in accelerating the reaction, causes this process to progress. A high yield of methyl esters can be produced through transesterification by carefully regulating the different factors that govern the process. These variables include the catalyst dosage, the proportion of alcohol to oil, the reaction temperature, and the reaction period (Du *et al.*, 2008). There are two methods that have been suggested for trans-esterifying vegetable oils to produce biodiesel. Enzymatic transesterification is carried out in a non-aqueous environment in the first method, which uses lipase as the catalyst. The second method is chemical, including the use of methanol or ethanol to treat extracted oil in the presence of a potent acid or base.

Uses of Bio-oils

Combustion Fuel: Utilized in boilers, furnaces, and engines for heat generation and power production.

Transportation Fuel: Can serve as a substitute for diesel after appropriate upgrading.

Chemical Production: Acts as a raw material for adhesives, phenol-formaldehyde resins, and various specialty chemicals.

Food Industry: Employed for producing liquid smoke and wood flavors.

Biotechnology: Potential for manufacturing anhydro sugars like levoglucosan, useful in pharmaceuticals and biodegradable polymers.

Upgrading of Bio-oil

The quality of bio-oils is often inferior to that of petroleum fuels, necessitating various upgrading techniques to enhance their properties.

Hydrotreating: Hydrotreating is a hydrogenation process that improves bio-oil quality by removing oxygen while maintaining the boiling range. Key aspects include:

Conditions: Mild, with catalysts such as $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$.

Drawbacks: Produces char, coke, and tar, leading to catalyst deactivation and reactor clogging.

Hydro-cracking: Hydro-cracking employs high temperatures and pressures, utilizing dual-function catalysts to facilitate cracking and hydrogenation. Key points include:

Conditions: Requires severe conditions (≥350°C, 100-2000 psi).

Advantages: Effective in producing light products, but can lead to high rates of cracking, resulting in the degradation of bio-oil to lighter gases and carbon.

Yield: Studies show oil yields ranging from 14-23 wt%, with significant carbon formation affecting overall efficiency.

Environment and Economic Consideration

The energy required to create biofuels must be considered when assessing their economic and financial benefits. Fossil fuels are used in the production of fertilizer, farming machinery, corn transportation, and ethanol refinement during the process of cultivating corn for ethanol. The energy gain from maize ethanol is typically negligible compared to that from sugarcane, cellulosic ethanol, or algal biodiesel, which may be much more apparent. When evaluating the advantages of biofuels, land use is another crucial factor. A debate regarding "food versus fuel" was sparked by the use of popular feedstocks like corn and soybeans as a primary component of first-generation biofuels. By diverting agricultural land and feedstock from the human food chain, biofuel production can change the economics of food availability and price (Janda *et al*., 2012). Additionally, energy crops created for biofuel could compete globally for regional environmental features. One fascinating advantage concerning biofuels is that, when combined with an new technique known as carbon capture and storage, production, and utilization Biofuels might be able to eliminate One of the atmosphere's greenhouse gases is CO2. Carbon dioxide would be extracted from the atmosphere when crops for biofuel expanded and caught during the burning of biofuels to create energy facilities that use electricity. It is possible to store carbon dioxide that has been trapped in the environment in solids like carbonates, deep sea silt, or geologic formations beneath the earth's surface.

Conclusion

Fossil fuels are expected to be severely scarce in the near future, which will have serious environmental repercussions. Consequently, it is essential to have a clean, sustainable alternative energy source. Fusion, wind, solar, and tidal energy are among examples. Depleting non-renewable energy sources combined with stringent environmental norms necessitate researchers to search for alternative energy sources. Bio-oil, a promising alternative to crude oil, can be produced from biomass using flash pyrolysis and hydrothermal liquefaction. Despite growing interest due to rising fuel costs, challenges such as high production costs, low yield, and poor quality persist. Bio-oil, although rich in chemical species, is primarily used as fuel oil, due to its greater calorific power when compared to the biomass from which it is made. Further research should concentrate on increasing oil yield and creating methods for turning pyrolysis oils into chemicals and biofuel. Bio-oils are a promising renewable energy source with a wide range of uses. However, in order to improve fuel quality and increase their applicability across a range of industries, their intrinsic qualities require considerable updating. The efficient use of bio-oils as sustainable energy sources will depend on ongoing research and development in improving technology.

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