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Lubricants from Biomass

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Abstract

Biomass is any organic material obtained from plants or animals. Moreover, biomass can be converted to other usable forms of energy and is an attractive alternative to oil because it is a renewable resource that is uniformly distributed over the surface of the Earth and is a source of energy that can be exploited using technologies environmentally friendly. In this article, the feasibility of production of lubricants from biomass with all its pros and cons will be analyzed. First, some incentives to produce bioproducts and principles of bioproducts will be mentioned. Moreover, the drive from the society to implement this "green" alternative will be explained; also, there are certain examples of actual use of lubricants from biomass. In relation with the elaboration process, the origin of the rawmaterials, the synthesis and the environmental impact will be analyzed. Finally, some conclusions about the development of bioproducts will be stablished.

Keywords: Lubricants, biomass, green chemistry, energy, synthesis

1. Incentives to Produce Bioproducts

In these days there are incentives (besides the environmental topic) that are arousing interest in the production of bioproducts from biomass:

i. Economic issues, because is cheaper to gather biomass, because is everywhere.
ii. The synthesis of new products with unique properties which do not have synthetic counterpart.
iii. The synthesis of high-added value products with "bio" or "natural" label, very attractive for marketing purpose.

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iv. The development of bioproducts requires less legislative constraints. Thus, biopolymers, even chemically modified, are presently exempted from the European REACH registration [1].

2. Principles of Green Chemistry

There are some principles of green chemistry which apply to this topic:

i. Design for energy efficiency. - Because energy from biomass is renewable and the processes where the biomass is used can be energy efficient. For example, to achieve biomass conversion to chemicals, a process-driven approach whereby biomass is converted by one or more catalytic processes (hydrogenation, hydrogenolysis, oxidation, etc.) yielding a family of valuable products. Thus, this approach is not intended to duplicate chemicals currently produced from fossil resources and could be more effective to find rapidly new valuable bioproducts [2].
ii. Use of renewable feedstocks. - It has now become more urgent to search for renewable feedstocks both for material and fuel, in fact, the major renewable feedstock on the planet both for material and energy is biomass, this includes wood, crops, agricultural residues, food, etc. Also, the reuse of waste from the bio-industries should provide a large amount of raw materials to replace the current petroleum feedstocks [2].

3. Drive from Society to Implement this "Green" Alternative

The multi-million tons lubricant market is traditionally based on mineral oils derived from petroleum. Because a large part of them leaks in the environment, regulations have been established in most countries to favour the use of lubricants based on renewable fatty compounds because of their biodegradability and absence of ecotoxicity.[1] Furthermore, The European Inventory of Existing Chemical Substances (EINECS) included 1,035 petroleum-related substances out of the 100,000 currently listed. The *DangerousPreparations Directive* covered mixtures of two or more substances, as defined by the European Community (EC). All preparations had to be assessed for toxicity and detailed records kept, additionally, detailed data sheets will have to be compiled for anything which could have an EINECS number, with full references so that the EC can check them, within six months of marketing where volumes were high (greater than 1,000 tonnes/year). Severe penal sanctions were available for enforcing these regulations.

Therefore, the sale of bioproducts would have fewer problems with the regulations and with the control of substances hazardous to health.

4. Real-World use of Lubricants from Biomass

Colin Brown of Samuel Banner Ltd, Liverpool, Britain's major independent vegetable oil refiner, gave an insight into the world of natural oils. All UK vegetable oil producers are members of Seed Crushers and Oil Processors Association (SCOPA) which provides a link between growers and refiners. Rape seed represents 50 per cent of UK production, followed by soya and sunflower. In the USA soya is the chief vegetable oil produced, with palm oil predominating in the Far East, while the French prefer sunflower oil. Lubricants are only a small market for vegetable oils in the UK. Probably the best known is castor oil, mainly glycerol tririncinoleate, which gave its name to Castrol, one of the major lubricating oil manufacturers. [3] And in Germany there are companies like Environmentally Friendly Lubricants and Carl Bechem GmbH in which only one-half of its products are mineral oil based, the rest are made from natural, polyglycol, ester, perfluoroalkylether, and other base stocks. Bechemspecializes in investing in niche markets. Analyzing the German market, one can observe that the production of lubricants from natural sources is taking place on an industrial scale, because they annually consume 1.5 million tons of lubricants, the breakdown is as shown in Table I. Also, the demand for biodegradable lubricants will be distributed as shown in Table II. Thus, for the cases presented, it can be said that the industrial scale production of lubricants from organic matter is a reality and other countries may follow this trend.

Table I: Breakdown of Types of Lubricant Used Annually in Germany

Types of Lubricants	Tonnes
Automotive	690000
Industrial, process and metalworking	830000
Grease	35000

Source: Wilson, B. B. (1991)

Table II: Demand for Biodegradable Lubricants in Germany

Biodegradable Lubricants	Thousands of tonnes/annum
Two-stroke engines	50
Chainsaws	9
Anti-corrosion oils	8
Wire rope	2
Mould and die release oils	10
Railway switchplates (points)	1

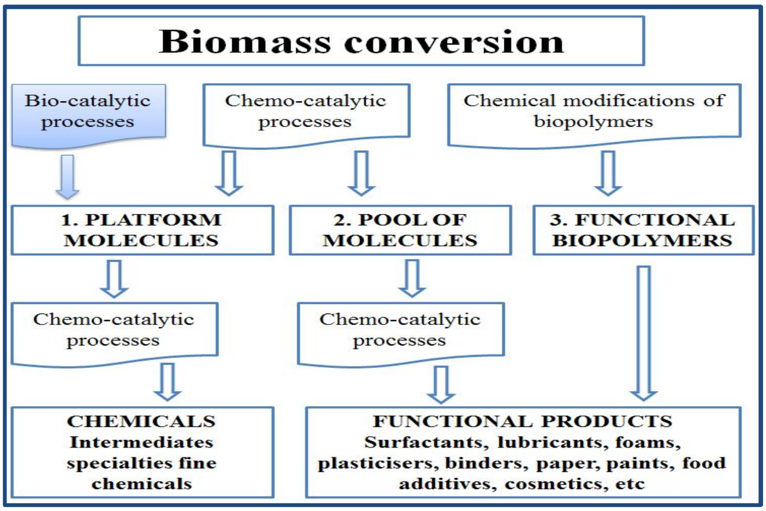
Source: Wilson, B. B. (1991)

5. Process Flowsheet

This paper focuses on the production of lubricants, so the focus will be in the obtaining of functional products. There are two ways to produce this kind of products [1], as it's shown in fig 1:

1. Biomass is converted in one or few steps to a mixture of molecules with similar functionalities that are used without separation for the manufacture of high tonnage end-products.
2. Biopolymers are chemically modified in one step to introduce new functionalities along the polymer backbone.

Fig. 2: Strategies of Biomass Conversion Processes



Source: Gallezot, P. (2012)

One bottleneck in this process occurs when unsaturated triglycerides and the corresponding fatty esters are obtained by transesterification, also it's known that in the presence of acidic or basic catalysts these have lubricating properties, however they are not stable to oxidation, exhibit a poor coldflowbehavior and should be modified to meet all specifications such as viscosity or shear stability needed for applications. Thus, antioxidant/antiwear additives could be used to improve their properties; however, this operation requires the use of time and raw materials, consequently, is an impediment which has to be overcome.

6. Raw materials

According to Metzger and Meier [4] oils and fats are the most important renewable feedstocks processed in the chemical industry. The annual production of plant oils attains 133 Megatonnes from which 107 Mega tonnes are employed to cover food needs and the rest is used for bio-diesel production (11 Mega tonnes), and other industrial uses (15 Mega tonnes) including oleochemical production.[1]

One major criterion for the choice of raw materials is their availability and cost because the targeted production of bioproductsshouldbe commensurate with available resources. Starch and other polysaccharides obtained from food crops provide a large source of C6 sugars. [5] Furthermore they could be replaced in the near future by cellulose which will provide an almost unlimited source of C6 without affecting food needs. In the same way hemicellulose, which is more easily depolymerised than cellulose, provides a potentially large source of C5 sugars. Vegetal proteins and aminoacidsobtained as co-products of carbohydrate fermentation to bioethanol could become a significant resource in the future

7. Synthesis

As mentioned above, to improve the lubricating properties of fatty esters it is common to use antioxidant additives, nevertheless, the properties can also be enhanceby adding new functionalities by reaction with the CQC bonds. Various types of oxidation of CQC bonds were described; but epoxidation followed by aperture of the oxirane ring with alcohols or acids was widely employed. The most common method used in industry to synthesizeepoxidised methyl oleate, linoleate, linolenate and commercial soybean oil was the epoxidationof fatty compounds with performic acid generated in situ by the reaction of hydrogen peroxide with formic acid. [1]

Flexible catalytic processes are needed to cope with variations in feedstock availability and molecular structure. Robust and easily regenerated catalysts should be developed because natural raw materials may contain impurities which could alter their selectivity and decrease their activity thus hampering catalyst recycling or continuous processes. New reaction media such supercritical fluids and activation systems (ultrasounds, microwaves) should be employed.

8. Waste Generation and Environmental Impact

The combustion of biomass produces particulates and polluting gases, it is known that in addition to CO2, the emitted particles are: polycyclic aromatic hydrocarbons, nitrous oxide, sulfur oxide (mainly coal) and carbon monoxide (CO), all of them cause adverse health effects. For the CO, the EPA[2] proposed maximum permissible values of 9 ppm (or 10mg/m3) in eight hours (USEPA[3], 1997).However, biomass conversion processes achieved in one or few steps without separation of intermediates are certainly more performing in terms of biomass utilization and waste minimization than the more traditional approach via platform molecules. [1]

At the present time, biomass is considered as the second source of ecology energy and sustainable in the market, after solar energy. Thus, its use represents a large number of advantages, both for the producer and for society and the environment.

Advantages:

- In the combustion process produces insignificant amounts of sulfur and ash so it does not cause the phenomenon of acid rain.
- Energy crops require less fertilizers and herbicides.
- For many industries or firms, the possibility of using their own waste to supply their own energy needs represents savings.
- It's a local energy source and contributes to the creation of new jobs.

2 EPA: US Environmental Protection Agency
3 USEPA: United States Environmental Protection Agency

Nevertheless there are some disadvantages that are worth to mention:

- Industrial facilities prepared for the use of biomass require an investment between 20% and 100% higher than those using fossil fuels.
- The storage of biomass requires much space.
- The costs of collection and preparation raise the price of this energy.
- The treatment of biomass generates a certain amount of pollutants that are hazardous to health. For instance: MSW incineration, biogas production, etc.

Some of these disadvantages can be minimized, like the space for storage, because some techniques for the efficient flow of materials can be used and a good plant distribution can be implemented, in order to improve the utilization of the space. Moreover, the disadvantages that are related with costs and prices can be reduced with a good industrial economic management.

9. Conclusions

The development of bioproducts at a large industrial scale requires that their quality and cost meet consumer demand. The final cost of bioproducts includes the price of the starting feedstock, but it also depends heavily upon the processing cost. The latter may be decreased by reducing the number of synthesis steps and improving their yields, but a judicious choice of biomass conversion strategy could be essential to achieve a cost-effective development of biomass utilization towards bioproducts. This value chain is environmentally and economically sustainable because it requires only a small number of conversion steps from raw biomass to end-products. One-pot processes could lead to a faster development of biomass utilization for the manufacture of industrial products while conversion processes via platform molecules have to compete with well-established current processes for the production of isolated, pure chemicals. The sustainability of biomass conversion processes can be evaluated by life cycle analysis (LCA) with a cradle-to-grave or cradle-to-gate approach which requires the inventory and environmental impact assessment of all inputs and outputs of the production system. Finally, I am convinced that production of lubricants from biomass is a promising and sustainable industry, which could leave great revenues in the close future.

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