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Review of biodiesel synthesis from waste oil under elevated pressure and temperature: Phase equilibrium, reaction kinetics, process design and techno-economic study

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ABSTRACT

The synthesis of biodiesel under elevated pressure and temperature could be promising technology which could result in sustainable biodiesel production, from renewable and waste streams like waste oil or used frying oil, thereby having no impact on biodiversity and the environment. This paper is comprehensive review of biodiesel synthesis from waste oil under elevated pressure and temperature: the supercritical or subcritical conditions of alcohol, with or without the use of heterogeneous catalyst. The review compromises the thermodynamic data, phase equilibria, phase composition and distribution during reaction, kinetic parameters and kinetic modeling, are presented. This type of data is necessary for process design and optimization. Process economics is analyzed and the impact of different production parameters (feedstock type, process parameters as temperature, pressure and alcohol to oil ratio, and different technology) is summarized and discussed.

Contents

1. Introduction

Biodiesel, defined as a mixture of monoalkyl esters of long chain fatty acids (mainly the fatty acid methyl (ethyl) esters or FAME (FAEE)) derived from a renewable lipid feedstock, such as vegetable oil or animal fat, is most commonly used renewable biofuel for internal combustion engines. The main advantage of the application of biodiesel fuel in the internal combustion engines is better quality exhaust gas emissions and the fact that it does not contribute to a rise in the level of carbon dioxide in the atmosphere. In addition, biodiesel has a relatively high flash point

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(average value of 150 °C), which makes it easier for handling, transport and storage and its biodegradability contribute to environmental safety. However, the most important advantage of biodiesel fuel is its production from renewable sources and its contribution to the sustainable energy supply [1,2]. Although a large-scale production of biofuels could cause biodiversity loss, conflicts with food security and increasing of net greenhouse gas emissions, small-scale production of biofuels have been concerns about the sustainability.

The International Energy Agency predicts that biofuels will provide approximately 27% of the world transport fuel by 2050 but currently biofuels provide only 2% of total transport fuel. These estimates are an integral part of current energy strategies for both developing and industrialized countries aiming to provide future abundant, cheap, renewable and environmentally friendly energy source [3]. In their report, Webb and Coates underline an important question: Even though much of the literature on biofuels implicitly assumes that biofuel is "renewable energy" and therefore an objective in itself, the issue is however, how does biofuel perform when compared to other renewable energy sources [4]? If a comparison between different renewable energy options is done in terms of arable land required to drive 100 km, the following results would indicate a striking differences between options: wind energy requires 1 m^2 of land, and hydrogen from lignocelluloses requires 5.3 m^2, while rapeseed biodiesel requires 53.6 m^2 [4]. Obviously, it appears that conventional biofuels offer some of the least land-efficient renewable energy sources [4].

Sustainability criteria and standards have already been integrated into certain voluntary certification schemes as well as national mandatory regulations, in order to prop-up sustainable biofuels. However, gaps in sustainability criteria and standards include cross-over effects with food sector, as well as environmental and social impacts. Further development and refinement of criteria is needed in order to have all possible relevant impacts properly evaluated, based on full life-cycle analysis (LCA). Most research results support approaches which improve the sustainability of agriculture as a whole, and not by sub-sector. Additionally, LCA′s of biofuels have to be improved and should take into account a broad range of assessment impacts along the life-cycle (farming, different feedstocks, and land use; techniques and practices; tailpipe emissions and consequences; biodiversity and more) [4,5].

Policy discussions over biodiesel and generally biofuels in industrially developed nations during 2012 have shown the increasing complexity of the topic. Originally promoted as a way of decreasing dependence on fossil fuels (from the perspective of oil importing countries) and avoiding the carbon emissions generated by them, biodiesel production has now been widely recognized to have strong impact on agricultural markets and even land-use patterns. Still high uncertainty that still remains over the impact of biofuels on food security and the environment, has made decision making complex and, in some cases, controversial. The optimal use of land, water and other resources depends on a country′s specific conditions and prioritized policy objectives. The development of biofuels in developing nations has been largely driven by Governments, through fiscal measures, subsidies and various other incentives, including trade policies. These measures have come under considerable scrutiny as they have resulted in debatable achievements. These incentives also usually fail to promote sustainability but they could be optimized to yield more positive outcomes. Financial support for biofuels that generate less environmental impact and less greenhouse gas emissions should be obviously prioritized, while focus of research and development of biofuels should target wastes and residues as primary feedstock [4].

Beside other limitation, the main obstacle for wider application of biodiesel is its relatively high cost. This is still the truth, although the price gap between petroleum based diesel fuel and biodiesel is narrowing due to the recent almost drastic changes of crude oil price (at the beginning of 2008–$150/bbl, the end of 2009–$40/bbl and the end of last year to $100–110/bbl). Such unstable price market of crude oil could be also expected in forthcoming years with tendency, as pointed out by many analyses at the end of 2012, to be very close to $250/bbl. This fact also requires that the overall cost of biodiesel fuel production needs to be reduced either by the reduction of raw material cost (vegetable oil, animal fat, and used vegetable oil), by decrease of utilities consumption (energy) and, of course, the application of more efficient processing technology taking into account its impact on the environment [6].

Waste cooking oil as cheep feedstock is produced around the world and developed countries produce million gallons of waste cooking oil per day. The large amounts of waste cooking oils are illegally dumped into rivers and landfills causing environmental pollution. The energy information administration in the United States estimated that around 100 million gallons of waste cooking oil is produced per day in USA. The per capita waste cooking oil production in Canada is approx. 9 pounds per year. In the EU countries, the total waste cooking oil production is approximately 700,000–1,000,000 t/year. The UK produces over 200,000 t of waste cooking oil per year. These quantities are sufficient for sustainable production of biodiesel if the collecting supply chain of waste cooking oil is operational [4,6,7].

The synthesis of biodiesel represents challenge for many researchers in the World requesting as main task determination the most economical and at the same time environmentally acceptable technology of production. Synthesis can be accomplished using several different technologies, therefore the selection of the most economical and at the same time environmentally acceptable production technology requires deep understanding of the underlying process phenomena. Application of supercritical alcohols (methanol and ethanol) for biodiesel production seems to be a potential solution which might fulfill both tasks [1,2,7,8]. The process does not require presence of a homogeneous or heterogeneous catalyst and proceeds at a very high rate. Moreover, the subsequent separation and purification steps are far simpler than in any other biodiesel processing technology. Subcritical transesterification is a promising method for a more environmentally friendly biodiesel production as a result of its feedstock flexibility, production efficiency and environmentally friendly benefits. Moreover, decreasing temperature and pressure, synthesis under subcritical conditions but with the aid of heterogeneous catalyst could also be the desirable technology for biodiesel production. The detailed techno-economic analysis was performed and will be underlined in this paper with comparison to conventional production.

The production of biodiesel fully compliant with EN 14214:2012 or ASTM 6751-12 is a very challenging task. To meet the both standards biodiesel should to have maximum 0.7% of glycerides and glycerol. Unconverted triglycerides, diglycerides, monoglycerides and glycerol, water and the other undesired components could cause significant engine damage and power loss. Therefore, the high conversion and purification steps are the most important for biodiesel production [9]. Regarding all this facts, and facts from previously published data, the synthesis of biodiesel under elevated pressure and temperature could be the only promising technology which could produce biodiesel in a sustainable way using renewable material from waste streams (from waste oil), thereby not impacting the biodiversity nor the environment in a negative way.

The aim of this paper is to summarize and to give comprehensive review of biodiesel synthesis from waste oil under elevated