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Modelling of an alternative process technology for biofuel production and assessment of its environmental impacts

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ABSTRACT

It is easy to predict that in the coming years in Europe biodiesel will play an increasingly important role in the transport sector. The European Commission has set at 10% by 2020 the proportion that biofuels should represent in total fuel used in transport and biodiesel is currently the most widely used biofuel in the European Union. The most common way to produce biodiesel is through transesterification of vegetable oils with methanol; glycerol is the main co-product. Although glycerol has many industrial applications, increased production of biodiesel could make complete market placement of this chemical difficult. In this context, increasing interest is paid towards different methods of biodiesel production that provide alternative co-products. This article offers a "cradle to gate" evaluation of potential environmental impacts caused by an innovative process for the production of DMC-BioD, an alternative biofuel to biodiesel which does not involve the production of glycerol. Transesterification of soybean oil with dimethyl carbonate to obtain DMC-BioD has been modelled with the aid of the Chemical Process Simulation software Aspen HYSYS® that produced the material and energy balances and the preliminary sizing of the process units. Results have been also compared with background information from database on the production of conventional biodiesel from soybean oil and of fossil diesel. The study suggests that DMC-BioD can be an interesting route for the production of biofuels from an environmental point of view. Compared to fossil diesel, GHG (Greenhouse gases) emissions can be decreased, although trade-offs are registered in other environmental categories. In any case, future investigation is needed in order to understand and optimize its environmental profile through the entire life cycle and possibly bring its production to a commercial scale. This preliminary analysis of potential environmental impacts provides useful information to continue the testing and scale-up phases and to improve the environmental performances of the process.

1. Introduction

The need to develop alternative energy sources is one of the most important priorities for the countries whose energy supply is heavily dependent on fossil fuels. In Europe, about one-third (31.6%) of final end use of energy in the EU-28 in 2013 is associated with the transport sector and it greatly contributes to the emission of pollutants and greenhouse gases (Eurostat, 2014).

Growing concerns about air emissions and fuel supply are encouraging to focus on biofuels (mainly biodiesel, bioethanol, ethyl butyl ether) as an alternative to fossil fuels (CORDIS, 2010). The European Commission has adopted a package of measures on renewable energy and climate change (Regulation EC 443/2009, Directive 2009/28/EC, Directive 2009/29/EC, Directive 2009/30/EC, Directive 2009/31/EC and Decision 406/2009/EC) aimed at reaching a market share of 10% of biofuels on transport fuels by 2020. From the environmental point of view, it is now well recognized that the potential benefits and impacts vary considerably depending on the type and source of biofuel (Zah et al., 2007; Naik et al., 2010; Dutta et al., 2014). The Directive 2009/28/EC requires

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List of acronyms and abbreviations

ADP	Resource depletion, mineral fossil and renewable
AP	Acidification
CPS	Chemical Process Simulation
DMC	Dimethyl carbonate
EtOH	Ethanol
FAGCs	Fatty Acid Glycerol Carbonates
FAMEs	Fatty Acid Methyl Esters
FEP	Eutrophication aquatic
FETP	Ecotoxicity (freshwater)
GHGs	Greenhouse gases
GWP 100	Climate change
HTPce	Human toxicity cancer effects
HTPnce	Human toxicity non-cancer effects
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LHV	Lower Heating Value
MeOH	Methanol
ODP	Ozone depletion
PAHs	Polycyclic Aromatic Hydrocarbons
PFD	Process Flow Diagram
PMP	Particulate matter/Respiratory inorganics
POP	Photochemical ozone formation
TAGs	Triglycerides
TEP	Eutrophication terrestrial
VOCs	Volatile Organic Compounds

that the savings in terms of greenhouse gas emissions from the use of biofuels and bioliquids – relevant for mandatory biofuel quota or for being eligible for financial support schemes – shall be at least 35% lower than fossil fuels. This reduction target will rise to 50% in 2017.

Biofuels refer to liquid, gas and solid fuels derived from biomass and are classified as first (from crop based feedstock), second (from non-food feedstock), third (from algae) and fourth (from genetically engineered crops) generation fuels on the basis of the biomass origin and production technology (Dutta et al., 2014). Currently, the trend is towards second generation biofuels, since the use of crops for biofuel cannot fully satisfy the present energy demand, also considering the current market price of crude and fossil fuels (Chauvet and González, 2008; Wiloso et al., 2012; Pereira et al., 2015). In addition, the replacement of first generation biofuels would allow avoiding the direct competition for the resource between food and energy markets (Cordella, 2010).

Biodiesel is the most common biofuel used in Europe, where in 2014 its production capacity was calculated to be 23,093,000 tons (European Biodiesel Board, 2015). Biodiesel is a mixture of fatty acid methyl esters (FAMEs) produced from vegetable oils or animal fats by transesterification of triacylglycerides (TAGs, triglycerides) with an alcohol such as methanol (MeOH) or ethanol (EtOH). The transesterification reaction is conventionally conducted in stirred reactors, generally batch, by mixing the oil with alcohol and then adding the catalyst after reaching the preset temperature. The catalysts can be basic, acid or enzymes. Currently, almost all industrial production of biodiesel is base catalyzed, as it turns out to be economically more advantageous, since it requires lower temperatures and pressures and has a conversion rate of about 98% (Zhang et al., 2003; Biodiesel Technocrats, 2011; Camino Feltes et al., 2011). The most important co-product of this transesterification is 1,2,3-propanetriol, commonly called glycerol, marketed as glycerin (concentrated aqueous solution of 1,2,3-propanetriol). Glycerol has numerous applications, especially in the pharmaceutical and cosmetics industries. It is conceivable, however, that, with the increased use of biodiesel in the coming years, the placing on the market of massive stocks of glycerin will become problematic. In this context, growing interest is paid to alternative methods of biofuel production that provide different co-products.

Fabbri et al. (2007) have described an interesting production process for biofuel that avoids the formation of 1,2,3-propanetriol as co-product; this biofuel is referred to as DMC-BioD. The block diagram of the DMC-BioD production process is shown in Fig. 1. The production process involves the reaction between triglycerides and dimethyl carbonate (DMC) to produce a mixture of fatty acid methyl esters (FAMEs) and esterified fatty acids of glycerol carbonate (FAGCs) which can be jointly used for energy purposes. The occurrence of FAGCs in DMC-BioD has some detrimental effects on” flow properties with respect to MeOH-biodiesel, but the use of DMC-BioD as an additive for fossil diesel appears to be adequate for existing diesel engines” (Fabbri et al., 2007). The production of biodiesel using DMC has attracted interest in the literature (see the reviews by Lee and Saka (2010) and Calero et al. (2015)). A main advantage of DMC-BioD was identified in the incorporation of most of the glycerol (>65%) into the fuel (Fabbri et al., 2007); other advantages comprise the use of a less harmful reagent/solvent (DMC in place of MeOH), process improvement (e.g. catalyst separation) and formation of valuable co-products (glycerol mono and dicarbonate) (Rathore et al., 2015). Glycerol carbonate is a widely investigated compound for novel direct (as such) and indirect (as intermediate) applications (Sonnati et al., 2013). A more insightful comparison between conventional and glycerin-free biodiesel production can emerge from the quantitative evaluation of the environmental impacts associated with the two processes.

This study aimed at assessing the potential environmental impacts of the production process of DMC-BioD, comparing them to the production process of biodiesel through base catalysis. Flow and combustion properties of DMC-BioD, relevant for its application as a fuel, are in general rather comparable to those of conventional MeOH-biodiesel. Some of the observed differences can be rationalized by considering the presence of FAGCs, which have molar mass 86 Da larger than those of the corresponding FAMEs. In fact, vacuum distillation and flash point data support the occurrence of a less volatile fraction in DMC-BioD. Nevertheless, the cetane number, which is a measure of the time elapsed from

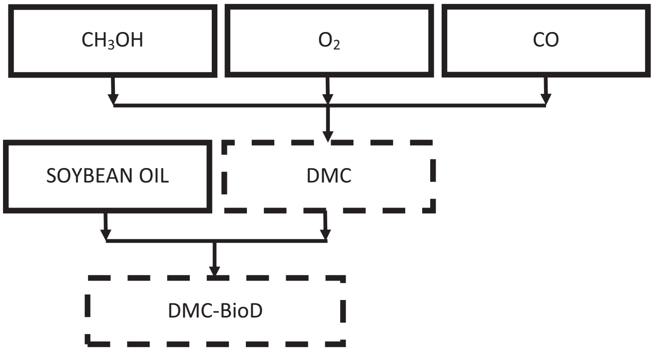

Fig. 1. Flow diagram of the synthesis process of DMC-BioD. Dotted boxes indicate the processes modelled through Aspen HYSYS®.

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