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Process sustainability of biodiesel production process from green seed canola oil using homogeneous and heterogeneous acid catalysts

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ABSTRACT

In this study, the sustainability of homogeneous and heterogeneous acid catalyzed biodiesel production process from green seed canola (GSC) is evaluated. The term "sustainability" is assessed based on four criteria, e.g. process economics, process safety, environmental impact and process energy efficiency. Based on the assessment, it is concluded that both the processes are economically profitable, when the cost of the feedstock is $ 0.35/kg. Heterogeneous acid catalyzed process shows higher profitability. Comparatively, heterogeneous acid catalyzed process is a safer process and creates less environmental impact. Additionally, heterogeneous acid catalyzed process is more energy efficient and more environment friendly than homogeneous process.

1. Introduction

Biodiesel is an attractive diesel substitute fuel because of its low emission profile and renewability. However, the biodiesel price is still expensive ($ 4.24/gal) as compared to the petroleum diesel fuel ($ 3.91/gal) [1]. Additionally, production process profitability is still being challenged due to higher feedstock price. On the contrary, cheaper feedstock is only compatible with acid catalyzed process because of the presence of high amount of free fatty acid (FFA). Especially, solid acid catalysts are desired because of easy product separation and waste minimization [2].

Green seed canola oil is one of the low quality cheap oils available in large amounts in Saskatchewan, Canada. The raw green seed canola oil cannot be used for edible purpose and the presence of high chlorophyll also negatively affects the oxidation stability of the oil [3,4]. However, a study showed that high quality biodiesel with improved oxidation stability can be produced from this oil using a novel catalyst, which acts as a chlorophyll absorbent along with its role as a catalyst [5].

Sustainability is a global and a very important issue for the long-term ecosystem and societal benefit, which demands minimum impact on the ecosystem during the manufacturing of any goods or substances. As criteria of sustainability assessment (Fig. 1), now a days, many researches include ecological and social indicators along with economic studies during the early process development and design stages [6]. From economic point of view, a process with positive or higher profit, net present value (NPV) and discounted cash flow rate of return (DCFROR), also known as internal rate of return (IRR) are considered to be economically feasible [6]. Ecological impacts are evaluated based on the environmental impacts and energy efficiency of the process (Fig. 1). An algorithm namely, waste reduction algorithm (WAR) is developed by US EPA [7] to assess the environmental impact at the manufacturing stage within the overall lifecycle of the chemical production and process. The energy efficiency of the process can be evaluated based on the energy of the raw materials and the products [8]. Social impacts are evaluated based on the possibility of the accident, explosion hazard, occupational diseases, toxicity of the process and materials. All these facts cannot be measured in numbers, however can be correlated with the chemical safety and the process equipment safety. Recently a comprehensive safety analysis method has been developed [9] to rank and score the individual equipment and overall chemical process by considering the facts of hazard from individual chemical, reactivity and explosion from the chemical mixture, flow rates, individual equipment operating capacity, temperature and pressure. Higher score indicates higher risks of accident associated with the process. This method provides detailed process safety information with minimal process information at the initial stage of design. An algorithm of sequential process sustainability study has been shown by Li et al. [6]. According to the algorithm, economic feasibility is conducted first. If it proves feasible, then the second stage is social impact analysis and the last stage is

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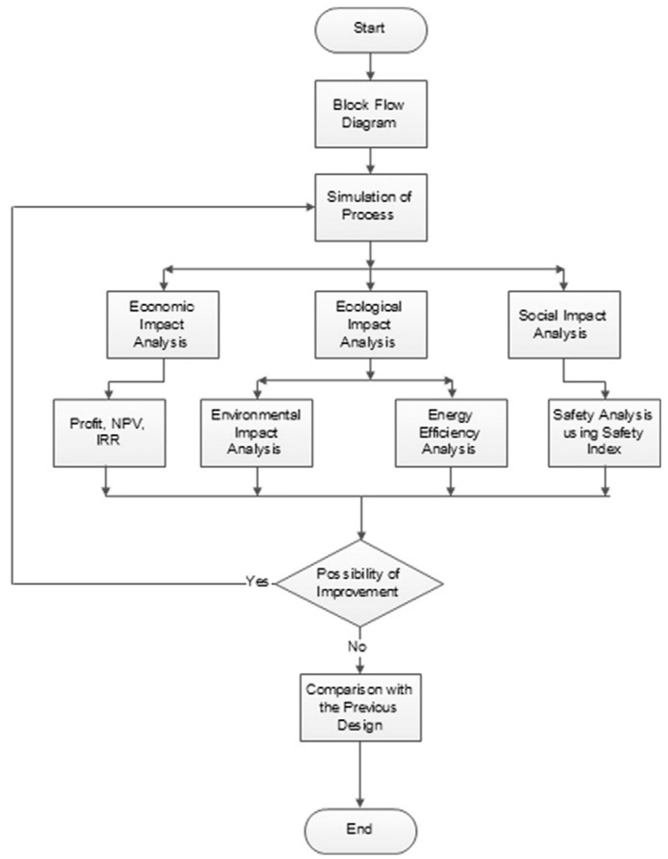

Fig. 1. Criteria for sustainability assessment.

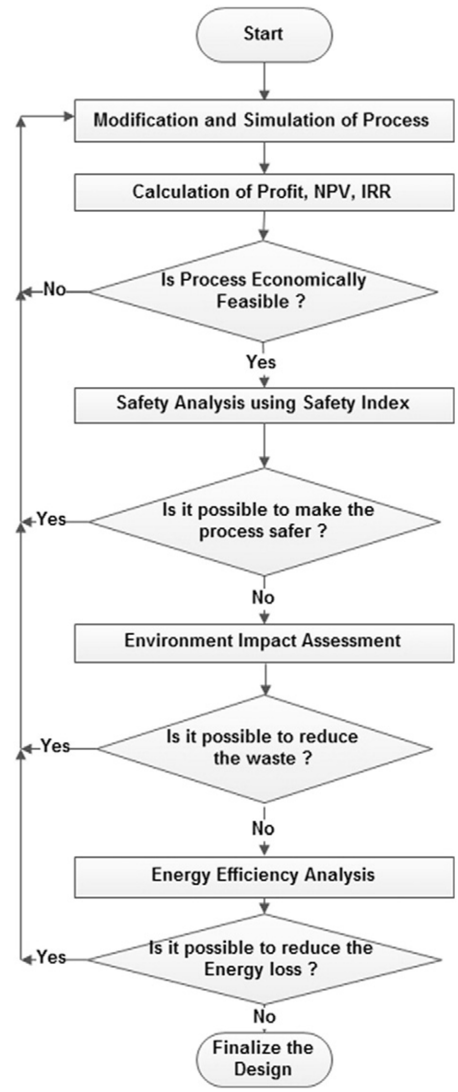

Fig. 2. Algorithm for sustainability analysis.

ecological impact analysis (Fig. 2). If all the criteria satisfy, then the new process and its design are finalized over existing conventional process.

Previous economic studies on biodiesel process show that one step homogeneous acid catalyzed process is more profitable than two step homogeneous acid and base catalyzed process [10,11]. It has also been demonstrated that heterogeneous acid catalyzed process is much more profitable compared to homogeneous acid catalyzed process if the operating conditions are close [11]. However, no literature is found on the process sustainability study of the homogeneous and heterogeneous acid catalyzed biodiesel production from the green seed canola oil. This research paper introduces for the first time the process sustainability study of green seed canola biodiesel production processes along with chlorophyll removal.

2. Development of process models

Aspen HYSYS v.2006 is employed to obtain mass and energy balance for simultaneous esterifcation, transesterification and chlorophyll removal of GSC oil process using homogeneous and heterogeneous acid catalysts and thereafter sustainability assessment are performed for the same systems. All the unit operations, input conditions and operating conditions are specified during process flow sheet development. Triolein, diolein, monoolein, oleic acid are selected to represent the triglycerides (TG), diglycerides (DG), monoglycerides (MG) and free fatty acids (FFA) of the GSC oil. In all the previous process feasibility analysis papers, the presence of DG and MG are neglected, even though the MG is present in case of incomplete conversion. In this paper in the process simulation, TG, DG, MG, solid catalysts, CaO, $CasO_4$, chlorophyll A and B (Ch-A and Ch-B) are inserted as hypothetical compounds. Thermodynamic group contribution method is used to develop and define the properties of TG, DG, MG as the hypothetical liquid compounds [12,13]. Chlorophyll A and B are treated as solids and the properties of solids and thermodynamics are obtained elsewhere [14,15]. The properties of other components (e.g. water, oleic acid, methyl oleate, glycerol, methanol) are collected from the HYSYS library. As the simulation involves polar components (glycerol and methanol), non-random two liquid (NRTL) thermodynamic model is chosen as the base model for the simulation of the biodiesel production process. Since some of the binary interaction parameters are not available in the databank, they are estimated using the UNIFAC vapor–liquid equilibrium and UNIFAC liquid–liquid equilibrium. Plant capacity is specified at 8000 tonnes/year (the same as in Zhang et al. [10]; West et al. [11]). This translates to vegetable oil roughly 1000 kg/h for process configuration. Gravity separation methods are used to separate the salts after neutralization in homogeneous acid catalyzed process and to separate the catalysts in the heterogeneous acid catalyzed process. Conversion reactors are used to represent the simultaneous esterification, transesterifcation and chlorophyll removal and also neutralization of the homogeneous acid catalyst with base. Similarly, conversion reactor is used to represent the simultaneous esterification, transesterifcation and chlorophyll removal for heterogeneous acid catalyzed process. In the simulation flow sheet, a dummy conversion reactor is used to represent the chlorophyll removal by the catalysts, even though practically transesterification, esterification reactions and absorbance occur in a single reactor. The reactors are assumed to operate continuously. For homogeneous acid catalyzed process, sulphuric acid (H_2SO_4) is used as the catalyst. The esterification,