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Cost analysis of enzymatic biodiesel production in small-scaled packed-bed reactors

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HIGHLIGHTS

- Cost analysis of 10,000 kg/yr of enzymatic biodiesel production in flow is studied.
- Parametric sensitivity analysis to study the effect of key variables on final cost.
- Case 2 – Increase in number of reuses of immobilized lipase is most profitable.
- Further improvement in key process parameters needed for industrial production.

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ABSTRACT

A cost analysis of enzymatic biodiesel production in small-scaled packed-bed reactors using refined sunflower oil is performed in this work. A few enzymatic micro-flow reactors have so far reached a performance close to gram-scale, which might be sufficient for the pharmaceutical industry. This study, motivated by the availability of new immobilization materials and techniques, wants to go one step further and explore the application of enzymatic micro-flow reactors to the biofuel market, which is much larger in volume. However, there are certain hurdles which need to be overcome to ensure commercialization of this process; this requires a simultaneous multi-innovation approach, which has been reviewed in the introduction. A detailed analysis of the two main hurdles – lipase production & immobilization, and severe mass transfer limitations – along with the state-of-the-art, and forecasted innovations, has also been provided.

The basic input data for the cost evaluation was taken from performance data of enzymatic micro-flow reactors published in literature, and certain assumptions (based on this data). The costs of enzymatic biodiesel production are also benchmarked against those of a real biodiesel production plant. It is found that a major cost for the scaled-up flow case is the enzyme cost. This is intrinsic to the approach adopted here; it adds process intensification value (here towards new resources: waste oils), and has to be accepted. Yet, an even bigger cost issue is the support material itself. The current costs of the commercial available Eupergit CM polymeric resin may allow its use in pharmaceutical manufacturing, but are prohibitively high for large-volume biodiesel production. The use of a similarly-functional polymer, which is simple to manufacture and lower in costs, is strongly advised, and we have chosen the SEPABEADS EC-EP/M carrier for this. An optimistic scenario is proposed with the following assumptions: use of the cheap SEPABEADS EC-EP/M carrier, utilization of refined sunflower oil as raw material, improved immobilization efficiency in regard to higher activity retention and enzyme loading, and increase in number of reuse of immobilized lipase. Following this, a production scenario for the enzyme-based biodiesel processing using refined sunflower oil at 10,000 t/a capacity can be made using 32 parallel reactors with 10 cm diameter and 100 cm length.

1. Introduction

Increasing prices of petroleum, diminishing crude oil reserves, a surge in the demand for petroleum-based fuels in transportation, as well as ever-growing environmental concern about the toxic effects of combustion products have led to the development of new,

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environmentally-friendly, alternative and renewable fuels, mainly biodiesel and bioethanol. Biodiesel plays a major role in this aspect due to its biodegradability, renewability, low emission profiles and non-toxicity [1–3]. Biodiesel is comprised of monoalkyl esters of long chain fatty acids derived from vegetable oils, animal fats, waste cooking oils, or micro algal oils. Owing to its properties which are similar to petroleum-diesel, such as cetane number, viscosity and energy content, it can be used directly as an alternative without the need to modify existing diesel engines and petroleum-based fuel distribution infrastructure. Additionally, biodiesel has a higher flash point which makes it a safer fuel to transport, store and use [2,4,5].

Biodiesel can be made via three different production processes: micro emulsification, pyrolysis, and esterification (also known as intra-esterification or transesterification). Transesterification of vegetable oils and animal fats with alcohol, in the presence of a catalyst (homogeneous or heterogeneous) has shown to be the most cost-efficient route for biodiesel production [6,7]. Conventional biodiesel production utilizes homogeneous catalysts (acid or alkali) in the transesterification reaction of high-quality oils with methanol, where biodiesel and glycerol are obtained [8]. Alkali-catalyzed transesterification is widely implemented on an industrial scale due to fast reaction rates, low cost of alkali catalyst (mainly NaOH and KOH) and methanol, moderate operating temperatures (60–80 °C), and high conversion. Here are a few disadvantages of the alkali-based process – this includes the undesirable saponification side reactions that lead to the formation of emulsions, lower ester yield and cause difficulties in biodiesel purification [9]. Acid-catalyzed transesterification requires more catalyst – sulfuric acid being the most common – but performs better at higher alcohol-to-oil ratios. On the downside, more process steps are required in acid-catalyzed production, which is more energy and economically demanding. Reaction rates are slow, and the use of acids can cause equipment damage. Additionally, huge amounts of wastewater are generated during chemically-catalyzed biodiesel production [2,4,10,11].

The afore-mentioned problems of conventional biodiesel production via chemical catalysts can be minimized or even eliminated by the application of lipase-catalyzed biodiesel production. As compared to chemically-catalyzed biodiesel production processes, enzymatic processes require less energy consumption due to milder reaction temperatures. Oils from different sources, as well as unconventional feedstock, such as waste cooking oil and microalgae oil, can be used as raw materials, since both triglycerides and free fatty acids are converted to biodiesel. There is no generation of undesired by-products, product separation and purification is easier, high quality glycerol is produced, and no wastewater is generated [2,11–14]. All these points contribute to lowering the cost of enzymatic biodiesel production, due to reduced energy consumption and high selectivity, and generation of a valuable by-product (glycerol, which can be separated without difficulty) [15].

However, there are certain disadvantages of the lipase-catalyzed process which constrain its implementation on an industrial scale. These include activity loss, high cost of enzyme (lipase), slower reaction rate, and inactivation by short chain alcohols and phospholipids. Thus, a multi-innovation approach is required to address the drawbacks. The essential innovation drivers for this approach (and their developments) are discussed hereafter.

The main impediment to the commercialization of this type of process still remains the cost of lipase production [16,17]. Thus, our discussion begins here. In order to overcome the problems associated with enzymes, and to make the process less cost-intensive, the implementation should ensure the immobilization and reusability of the enzyme [2,4,9,11,14–18]. Immobilization provides shorter reaction times, stability towards temperature, prevents chemical and shear denaturation, assures operational flexibility, and improves separation and reusability of the enzyme [2,11,19]. A number of techniques are available for lipase immobilization, such as adsorption, covalent binding, encapsulation and entrapment, on a variety of natural and synthetic supports. The selection of the support material depends on its flow properties, stability, availability, toxicity, hydrophobic/hydrophilic character and maximum loading capacity. The source of the lipase, reaction and process conditions determine the choice of a suitable immobilization process and the carrier [4,16,20].

High biodiesel production rates and catalytic activity have been reported from lipases originating from different microrganisms such as *Candida antarctica, Candida rugosa*, *Cryptococcus* sp., *Trichosporon asahii* and *Yarrowia lipolytica* [21,14]. Moreover, in the past 20 years, microbial lipases – specifically to catalyze the methanolysis reaction, while not being strongly affected by the methanol in the reaction mixture – have been determined [15].

Lipases have also become more stable, thanks to pre-treatment procedures, selection of appropriate immobilization procedures (as mentioned above), and the use of whole-cell biocatalysts. Whole-cell biocatalysts ensure that the biocatalyst is active for a longer period of time, and there is no need for downstream processing of the enzyme, which is beneficial [14,17].

Additionally, efforts to counter the adverse effects of methanol have resulted in the use of alternative acyl-acceptors – such as higher or branched alcohols, and esters – which has resulted in a more active biocatalyst, better fuel properties and by-products [14].

Also, other aspects such as lipase specificity, oil composition and purity, oil to acyl acceptor molar ratio, temperature, and water content have been enhanced [22,23]. Various methods have been used to influence these factors – some of these are enzyme pretreatment and post treatment, techniques for methanol addition to reduce the adverse effects of methanol (step-wise addition of methanol in single-step, two-step or three-step reactions), use of solvent and silica gel, novel reactor designs (process intensification by using Oscillatory Flow Reactor, Ultrasonication, Microwave) and employing a combination of lipases. Genetic engineering technology can also be employed to develop lipases that are more stable in the presence of methanol.

Another factor which can reduce production costs is the use of low-grade oil (such as cooking oil), instead of pure oils, which are more expensive [9]. However, this might be a disadvantage, since the free fatty acids (FFA) in waste cooking oils are high.

Still, when it comes to industrial biodiesel production, the application of immobilized lipases has its disadvantages, like partial activity loss due to the rigorous immobilization protocol, mass transfer limitations and glycerol deposition on the surface of the immobilized lipase [20]. Nevertheless, the advantages of immobilized lipases open new doors to reach potentially cost-effective, environmentally-friendly, continuous industrial biodiesel production.

However, significant efforts are required in order to reach economically viable, industrial-scale applications [1,13,24]. Balcão et al. [25] have published a detailed review on different immobilization methods and reactor configurations with the use of lipases, such as batch-stirred tank reactors (STR), packed-bed reactors (PBR), fluidized-bed reactors (FBR) and membrane reactors (MBR). Amongst these, STRs are used most frequently, since they are easy to operate. However, due to operation in batch mode, using an STR results in low volumetric productivity [2,18]. For two-phase (solid-fluid) reactions in heterogeneous catalysis, the most employed reactors are packed-bed reactors and are known to be more cost-effective than STRs [1,4,26,27].

Recently, enzymatic micro-flow reactors were introduced in bio flow chemistry aiming at preparative biotransformations and pharmaceutical manufacturing [28,29]. The immobilization measures for diverse enzymes on polymeric beads and other supports have been described in literature. Such loaded beads are filled into a tube reactor, thereby providing a packed-bed through which the reactant stream flows.

Production considerations of enzymatic flow reactors were reported by us [30,31], and for a broader picture, sustainability studies for biodiesel manufacture through process intensification were reported by another group [32,33]. Current enzymatic flow reactors [30,31] can reach a capacity performance close to gram-scale which makes them