Integrated Biodiesel Plants: Options and Perspectives

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In this study, we investigate the upgrading of biodiesel plants into integrated biorefineries. Economic analysis and a life cycle assessment studies have been implemented for an integrated biodiesel biorefinery using its side-product (glycerol) to produce succinic acid (SA), a value-added chemical. Four process scenarios considering different uses of glycerol are simulated in Aspen Plus and MatLab and compared in this study. We examine simple utilisation methods of this side-product such as the disposal, distillation (80%) and purification (95%) of glycerol and we compare them in terms of economic and environmental impact with an integrated approach that produces SA via fermentation. For the latter case, we have incorporated into the overall process a batch fermenter to convert glycerol into succinate followed by a purification/recovery process to produce pure SA crystals. Furthermore, we have performed optimisation studies to compute the maximum profit and simultaneously to reduce the environmental impact. Profitability indicators are used to compare the developed biorefinery cases while environmental impact is calculated based on the CO₂ emissions for each scenario.

1. Introduction

Recently, the demand for global transportation has increased significantly leading to an extensive global energy demand and consumption. The transportation market for vehicles is based on petroleum derivatives such as diesel and gasoline. Renewable fuels made from biomass like biodiesel and bioethanol can partially and/or entirely substitute the petroleum based fuels in internal combustion engines (Demirbas, 2008). Promotion of biofuels by governments and international unions target the substitution of gasoline and diesel by endogenous produced biofuels in order to create a petroleum-free market for their countries (Vlysidis et al., 2011). Biodiesel is mainly supported in EU countries and its production has received increasing interest the last ten years (Vlysidis et al., 2011). This biofuel is produced from the triglycerides found in vegetable oils and/or animal fats, which react with methanol to form fatty acid methyl esters (biodiesel) and glycerol through a simple chemical reaction called transesterification. Although conventional production methods for biodiesel require large expanses of land to cultivate the required crop seeds; innovative oil production methods that derive oil from algae or oleaginous yeasts have given new perspectives to this biofuel (Azócar et al., 2010). Even though biodiesel production has increased worldwide extensively, there are still sustainability issues in terms of economics to overcome. Biodiesel production costs
more than petroleum diesel. However, due to governmental tax support systems (Vlysidis et al., 2011) biodiesel production remains economically feasible. Therefore several techno-economic analyses on biodiesel industry have been developed examining its economic prospective and profitability (Zhang et al., 2003; Binns et al., 2011). Zhang et al. (2003) have used simulations in HYSYS to compare four different biodiesel processes by studying two different catalysts and two different feedstocks. Moreover, Hu et al (2007) have implemented life cycle analysis and economic assessment for soybean biodiesel and conventional biodiesel. They found out that even though the soybean biodiesel is cleaner and more renewable from diesel its price makes it economically unattractive. The main disadvantage of biodiesel over conventional diesel is that its production costs are higher due to the costs of the raw materials that are used (especially crop oil/seeds) which are much more expensive than the extraction costs of crude oil. The utilization of by-products from the biodiesel process can improve its economic sustainability. The transesterification process, co-produces glycerol, in addition to the biodiesel, that amounts to 10% of the total production. Johnson and Takoni (2007) have illustrated the different chemical/biochemical routes of glycerol to various commodity chemicals. Most of them are until now petroleum-derived. Recently, Vlysidis et al. (2009) developed an innovative biochemical method for adding value to glycerol by converting it via fermentation to succinic acid, which is considered to be a top value-added material for the production of several commodity and specialty chemicals (Werpy and Petersen, 2004). In this study, we compare different scenarios that utilise the glycerol produced from a biodiesel plant. We design an integrated biorefinery that produces biodiesel and SA, and compare it in terms of economics and emissions with simpler schemes that dispose, distil or purify the glycerol. Finally, to manage our system’s environmental impact we perform multi-objective optimisation to compute optimal profits while keeping CO₂ emissions at desired levels.

2. Methodology

2.1 Process Description and Plant Design

In this study, we design and simulate in Aspen Plus a small biodiesel plant that has an annual capacity of 7.8 kt of biodiesel, which corresponds to 1000 kg/h of crop oil. Figure 1 illustrates a feasible topology of an integrated biorefinery flowsheet for the co-production of biodiesel and succinic acid. Obviously other (rather similar) configurations are possible, however, detailed comparisons as well as additional options such as e.g. heat integration are the subject of a future publication. Fig.1-A depicts the biodiesel process starting from rapeseed oil; the latter has been obtained from a mechanical press and solvent extraction units that are not showed here. The unit configuration is similar to Zhang et al. 2003. In addition to the oil, methanol and catalyst (KOH) also enter into the transesterification reactor, which produces biodiesel and glycerol. To improve reaction yields we add a surplus of methanol, which is partially recovered (after the reaction) by a distillation unit. The catalyst is also being removed by neutralisation and the produced FAME is refined to reach the appropriate biodiesel specifications. The crude glycerol stream contains, apart from glycerol, a number of impurities including methanol, water traces of FAME and triglycerides.
Glycerol is diluted with water and sterilized and biomass enters the bioreactor by a different stream. Fermentation is simulated as a batch process using kinetics obtained from a previous study (Vlysidis et al., 2011a). Fig.1-C shows the downstream recovery of the desired product as described in (Vlysidis et al., 2011b). Biomass is removed by filtration while most of the water and by-products are removed by vaporisation. The wastewater is then distilled and recycled for reuse. Succinate is converted via crystallization to SA crystals, which are removed from the liquid and dehydrated. As
alternatives to SA, we have also considered crude glycerol distillation to 80 % and its purification to 95 % by adding a distillation column to the glycerol stream in Fig1-A.

2.2 Economic Analysis
The economic analysis of the plant consists mainly of the capital \( C_{\text{CAP}} \) and annual operating costs \( C_{\text{OPE}} \). The first one consists mainly of the equipment cost \( C_{\text{EQ}} \) with extra costs to cover installation, piping, buildings, auxiliary facilities and contingencies. The \( C_{\text{EQ}} \) has been calculated in a previous study of Vlysidis et al. (2011). The annual operational cost \( C_{\text{OPE}} \) consists of the utility costs \( C_{\text{U}} \), the wastes costs \( C_{\text{W}} \), the raw material costs \( C_{\text{R}} \) and several extra costs that are vital for plant’s operation \( C_{\text{EX}} \). \( C_{\text{R}} \) and \( C_{\text{L}} \) are calculated inside Aspen from the mass and energy balances respectively while \( C_{\text{EX}} \) is mainly consisting of the labour, maintenance and plant overhead costs. After the economic assessment of the above scenarios, comparisons are performed using common profitability indicators such as the Net Present Value (NPV), the internal rate of return (IRR) and the payback period (PBP) (Turton et al., 2009).

2.3 Optimisation studies
Optimisation studies were performed for the succinic acid scenario to maximise the NPV (Eq.1) (Turton et al., 2009) and/or minimise CO2 emissions. The two chosen optimisation bioprocess parameters are the water flowrate (kk1) entering the bioreactor and the fermentation cycle time (kk2). Both have a major effect on the capital cost of the fermentor, which is by far the most expensive equipment of the overall process.

\[
\max \, NPV(kk) = -C_{\text{CAP}} + P \left( \frac{(1+i)^Y - 1}{i(1+i)^Y} \right)
\]

(1)

Where: \( P \) is the annual net profit (Annual Revenues-C_{\text{OPE}}), \( i \) is the interest rate (7 %), \( Y \) is the lifetime of the plant (20 years) and \( C_{\text{CAP}} \) is the capital cost (Singhabhandhu and Tezuka, 2010). To maximize the profits while minimising the CO2 emissions we have performed multi-objective optimisation using Pareto curves (Azapagic and Clift, 1999). The CO2 emissions are dependent on the amount and type of energy consumed. Gas and electricity produce 0.201 and 0.537 kg-CO2/kWh. The objective function is the same as in eq.1 an additional bound for the amount of CO2 emitted. The above optimisation problems were solved using stochastic optimisation (simulated annealing) developed in MatLab and linked directly with Aspen Plus simulations.

3. Results
Results from the economic analysis and the profitability indicators for the four different cases are presented in Table 1. The succinic acid scheme has the highest capital and operating cost. It requires a much larger investment for its production and purification, more energy and labor to operate and higher cost to maintain the purchased equipment. As a consequence it has the highest unit biodiesel production cost. For the examined case \( i=7\%\), \( Y=20 \) y the optimized succinate scenario exhibits the highest NPV and PBP values. Its NPV value is 60 % higher than the base case scenario (Glycerol disposal) while the PBP is only 0.6 y higher. Although, the IRR is lower than those of other schemes it is considered to be an attractive investment as it is much higher than
the original interest rate (7 %). In Figure 2 the NPV for different interest rates is depicted. The succinic acid scheme is more attractive at rates below 12 % while it becomes unprofitable for rates higher than 17%. This graph also illustrates that purification of glycerol (95 %) can be a good solution for high interest rates.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Succinate</th>
<th>GLR (95 %)</th>
<th>GLR (80 %)</th>
<th>GLR Disposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{CAP}}$ (M.€)</td>
<td>10.7084</td>
<td>5.5100</td>
<td>5.4786</td>
<td>5.2794</td>
</tr>
<tr>
<td>Unit Production Cost (€/L)</td>
<td>1.0137</td>
<td>0.9038</td>
<td>0.9029</td>
<td>0.8976</td>
</tr>
<tr>
<td>Annual Revenues (M.€)</td>
<td>10.9821</td>
<td>9.3267</td>
<td>9.1732</td>
<td>9.1265</td>
</tr>
<tr>
<td>$C_{\text{OPE}}$ (M.€)</td>
<td>9.0325</td>
<td>8.0526</td>
<td>8.0445</td>
<td>8.0414</td>
</tr>
<tr>
<td>Annual Profits (M.€)</td>
<td>1.9496</td>
<td>1.2741</td>
<td>1.1287</td>
<td>1.0851</td>
</tr>
<tr>
<td>NPV (M.€)</td>
<td>9.95</td>
<td>7.99</td>
<td>6.48</td>
<td>6.22</td>
</tr>
<tr>
<td>IRR %</td>
<td>17.5%</td>
<td>22.7%</td>
<td>20.0%</td>
<td>20.0%</td>
</tr>
<tr>
<td>PBP (y)</td>
<td>5.5</td>
<td>4.3</td>
<td>4.9</td>
<td>4.9</td>
</tr>
</tbody>
</table>

For the two other scenarios (GLR 80 % and GLR disposal) we get much lower NPV than the first two schemes. The optimum parameter values for the SA case were 104 h cycle time and 79.7 kmol/h water flow rate. From the multi-objective optimisation CO₂ emissions were decreased by 6 % (6.4 kt-CO₂/y instead of 7.0 kt-CO₂/y) while only decresing the NPV by 2 %. The new parameter values were estimated to be 210 h cycle time and 71.80 kmol/h water flow rate. It becomes apparent that to reduce the environmental impact we need to use more concentrated solutions and to allow more reaction time for the fermentation process to consume the more dense medium.

![Figure 2: NPV values with respect to different interest rates for the four scenarios](image)

**4. Conclusions**

Utilisation of crude glycerol from biodiesel production can play a significant role in the biorefinery’s sustainability. We showed that glycerol can be used as a key renewable material for the production of value added chemicals like succinic acid. Optimisation
studies revealed that this option produces the highest profit (9.95 M€) when compared with the purification, distillation and disposal of the crude glycerol. Moreover, multi-objective optimisation lowered the CO₂ emissions by 6% while keeping the profits to almost the same levels. More (bio)-chemical routes of glycerol to chemicals should be explored so as to give further and better options towards biodiesel’s sustainability.

References


Vlysidis A., Binns M., Webb C. and Theodoropoulos C., 2011a, Glycerol utilization for the production of chemicals: conversion to succinic acid, a combined experimental and computational study, Biochemical Engineering.

Vlysidis A., Binns M., Webb C. and Theodoropoulos C., 2011b, A techno-economic analysis for upgrading the biodiesel industry to an integrated biorefinery for the co-production of fuels and chemicals, Energy.

Werpy T. and Petersen G., 2004, Top value-added chemicals from biomass Vol I-Results of screening for potential candidates from sugars and synthesis gas, US DoE