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Comparison between exergy and energy analysis for biodiesel production

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This study investigates the exergy concept for use in chemical engineering applications, and compares the energy and exergy methodology for the production process of biodiesel.

A process for biodiesel production was suggested and simulated in view of the energy and exergy analysis. A method was developed to implement the exergy concept in Aspen Plus 7.3. A comparison between the energy and the exergy approach reveals that the concepts have similarities but also some differences. In the exergy study, the reaction section has the largest losses whereas in the energy study separation steps are the most important. An optimization, using both concepts, was carried out using the same parameters. The optimized results were different depending on the objective function. It was concluded that exergy analysis is crucial during the design or redesign step in order to investigate thermodynamic efficiencies in each part of the process.

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1. Introduction

Predictions concerning the future energy demand indicate a major increase [1], thus the energy supply in the future is of major concern. For the moment, approximately 34% of this energy is delivered by liquid fuels (including biofuels) [1]. A recent estimate of British Petroleum claims that there is still enough oil for the coming 53 years [2]. It is however obvious that solutions for the oil depletion have to be found. A first approach to tackle the oil depletion problem is to increase the efficiency of the current production processes. This is not a solution to the problem itself but it allows the remaining oil to be used as efficiently as possible.

At present, most processes in the chemical industry are optimized based on the first law of thermodynamics since this enables engineers to determine the energy requirements. However, this does not indicate whether or not the energy is used efficiently. Introducing the second law of thermodynamics, it is possible to define differences in energy quality and to define efficiency. The more a process generates entropy, the less it will be thermodynamically efficient. Examining the extent of entropy generation provides a measure to investigate the efficiency of a process [3]. Entropy generation and lost work potential result in the property of exergy, which may be used to evaluate the efficiency of a process. Exergy represents the useful amount of work that can be extracted from a system when brought into thermodynamic equilibrium with the environment. An exergy analysis of a process allows to pinpoint the thermodynamic losses and inefficiencies of each unit appearing in the production process [3]. Therefore, exergy analysis seems to be a very efficient tool to improve the overall efficiency and to ensure the sustainability of the process as it provides a direct measure of the losses occurring in the system [4]. However, the number of exergy studies specific to the chemical industry is much lower than in other research fields. Less than 15% of the exergy analyses deal specifically with the chemical industry [5].

Along with the improvements of the efficiency of the process, the necessity to find alternatives for fossil fuels is nowadays very important, because of their demand and the consequent reserves. Biodiesel is a derivative of vegetable oils or animal fats that is used as fuel. Biodiesel is defined as the monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock [6]. Biodiesel is

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List of abbreviations

$\dot{n}_i$	Molar flow rate of stream [kmol/s]
h	Molar enthalpy [J/kmol]
V	Velocity [m/s]
g	Gravitational acceleration [m^2/s]
z	Height [m]
$\dot{Q}$	Heat transfer flow [W]
$\dot{W}$	Work transfer flow [W]
s	Molar entropy [J/(kmol K)]
P_0	Reference environment pressure [1 atm]
T_0	Reference environment temperature [298.15 K]
T_i	Temperature of heat source [K]
$\Delta\dot{S}_{irr}$	Entropy production [J/(K s)]
e	Specific exergy of a stream [kJ/mol]
$\dot{E}_d$	Exergy destruction [W]
b^o_{ch}	Standard chemical exergy [J/kmol]
$\Delta_f G^o$	Standard free Gibbs energy of formation
ν_{el}	Stoichiometric coefficient of element 'el'
$b^o_{ch,el}$	Standard chemical exergy of element 'el' [J/kmol]
e^{ch}	Molar chemical exergy of a stream [J/kmol]
x_i	Mole fraction [-]
R	Universal gas constant [J/(K kmol)]
b^{cho}_i	Standard chemical exergy of compound i [J/kmol]
γ_i	Activity coefficient of substance i [-]
φ	Chemical exergy relation [-]
$(NCV)^o$	Net caloric value [J/kmol]
h'	mass fraction of hydrogen in the fuel mixture [-]
c'	mass fraction of carbon in the fuel mixture [-]
o'	mass fraction of oxygen in the fuel mixture [-]
s'	mass fraction of sulfur in the fuel mixture [-]
e^o_C	Standard chemical exergy of carbon [kJ/mol]
$e^o_{H_2}$	Standard chemical exergy of hydrogen gas [kJ/mol]
$e^o_{O_2}$	Standard chemical exergy of oxygen gas [kJ/mol]
$e^o_{N_2}$	Standard chemical exergy of nitrogen gas [kJ/mol]
α	Number of carbon atoms [-]
β	Number of hydrogen atoms [-]
γ	Number of oxygen atoms [-]
δ	Number of nitrogen atoms [-]
η	Efficiency [-]
$\dot{B}_{...}$	Exergy flow associated with a stream [W]
$L\dot{W}$	Lost work [W]
T	Temperature [K]
$\dot{E}$	Energy [W]
MW	Molecular weight [g/mol]
RR	Reflux ratio [-]
$B{:}F$	Bottoms to feed ratio [-]
$D{:}F$	Distillate to feed ratio [-]
CSTR	Continuous stirred tank reactor
SQP	Successive quadratic programming
ExROI	Exergy return on investment
$\Delta reacG^o$	Gibbs free energy of reaction

also a much more environmentally friendly compound in comparison with its fossil counterpart. The combustion generates much less pollution and the emission savings are between 19 and 88%, depending of the sources of the raw material [7].

In literature, several processes are presented for biodiesel production [8–13]. Due to the different specifications of each process, i.e., the raw material, triglyceride, alcohol reactant, catalyst and especially the chemical and thermodynamic parameters, adopting a general process flowsheet is a difficult task. The main differences and contradictions are listed and discussed below:

- Reaction step: many process simulations use one reactor [8,14,15] (modeled by a yield reactor). Nevertheless, two CSTR reactors in series with an intermediate decanter are more realistic, since in industry the difference in density is extensively exploited.
- Methanol removal: in some works [8,14], the excess methanol is removed before the neutralization of the catalyst. This can shift the equilibrium of the transesterification towards the reactants which will decrease the biodiesel yield [16];
- Biodiesel temperature: Biodiesel is susceptible to thermal decomposition above 250 °C. In some works the bottom of the biodiesel distillation column attains too high a temperature value, up to 414.7 °C [8]. Therefore, the distillation column should be adjusted to a lower working pressure and a lower boil up rate to limit the temperature in the bottoms;
- Sequence of methanol-glycerol distillation: In some flowsheets, the glycerol is first purified to the desired grade and the top stream containing water and methanol is separated in a subsequent methanol distillation column [17]. In other flowsheets, the methanol is separated first as an almost pure stream and the bottoms containing water and glycerol is separated in a second glycerol distillation column [8,10]. In this work, the column sequence is investigated as a starting point of the energy analysis.

In the literature, several authors integrated the exergy equations in a simulator. Dudgeon used a technique based on 'USER2' blocks [18]. A second option found in the literature is Olexan [19]. ExerCom is a commercially available plug-in for Aspen and Pro/II [20]. The TAESS tool is another software used for the thermoeconomic analysis of energy systems to perform the exergy cost computation [21]. The program calculates the physical, chemical and mixing exergy based on Szargut's reference environment. Exergy is treated as an extensive stream property inside Aspen Plus. Abdollahi-Demneh et al. developed a method using user variables in HYSYS to calculate the exergy [22]. A very interesting coupling is the one presented in Ref. [23]. The authors propose the integrated use of Microsoft Excel and Aspen Plus, using a Visual Basic Application in Excel to do all the exergy calculations. In this work, another approach was used by means of the so-called 'Calculator blocks' in Aspen Plus.

Some exergy analyses of the biodiesel process have been carried out in the past, although based on different flowsheets. The exergy of a biodiesel process with Jatropha curcas as feedstock was investigated in Ref. [15]. In another work [14], a detailed exergy calculation of the process described by Zhang et al. Recently, an exergy analysis of the canola oil esters production was performed comparing the synthesis of methyl and ethyl esters [24]. In another work, the ExROI value (exergy return on investment) and renewable factor was calculated for biodiesel from cooking oil, demonstrating the better sustainability of this source compared to vegetable oils [25]. In this paper, an alternative biodiesel process was proposed and simulated in Aspen Plus, to clarify the different ways of biodiesel production. Afterwards the calculation of exergy was implemented in a comprehensible and user friendly way. Finally, the comparison of the exergy and the energy analysis was assessed.

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