Energy Conversion and Management 165 (2018) 183–194

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Exergoeconomic and exergoenvironmental co-optimization of continuous fuel additives (acetins) synthesis from glycerol esterification with acetic acid using Amberlyst 36 catalyst

Mortaza Aghbashlo[a,*], Meisam Tabatabaei[b,c,*], Hossein Jazini[d], Hassan S. Ghaziaskar[d]

[a] *Department of Mechanical Engineering of Agricultural Machinery, Faculty of Agricultural Engineering and Technology, College of Agriculture and Natural Resources, University of Tehran, Karaj, Iran*
[b] *Microbial Biotechnology Department, Agricultural Biotechnology Research Institute of Iran (ABRII), P.O. Box: 31535-1897, Agricultural Research, Education, and Extension Organization (AREEO), Karaj, Iran*
[c] *Biofuel Research Team (BRTeam), Karaj, Iran*
[d] *Department of Chemistry, Isfahan University of Technology, Isfahan, Iran*

ARTICLE INFO

Keywords:
Exergoeconomic analysis
Exergoenvironmental analysis
Fuel additive
Glycerol esterification
Multi-objective optimization

ABSTRACT

This study was aimed at comprehensively analyzing the exergoeconomic and exergoenvironmental performance of a continuous reactor applied to synthesize fuel additive (acetins) by glycerol esterification with acetic acid in the presence of Amberlyst 36 catalyst. The effects of various process parameters viz. esterification temperature, acetic acid/glycerol molar ratio, and reaction pressure on both exergoeconomic and exergoenvironmental variables were studied at a constant feed flow rate of 0.5 mL/min. In addition, an optimization study was conducted using response surface methodology (RSM) through minimizing both cost and environmental impact per exergy unit of the product. Overall, both acetic acid/glycerol molar ratio and esterification temperature had profound effects on the variables of both exergy-based methods, while reaction pressure trivially affected the output parameters. The optimum operating conditions were: acetic acid/glycerol molar ratio = 1.1:1, esterification temperature = 102.0 °C, and reaction pressure = 16.7 bar. Under these conditions, the cost and environmental impact per exergy unit of the product were found to be 218.11 USD/GJ and 171.40 mPts/GJ, respectively. Generally, noticeable differences were observed in the optimum operating conditions proposed based on the process yield compared with those suggested by the exergoeconomic and exergoenvironmental methods.

1. Introduction

Biodiesel is a promising substitute for crude oil-derived diesel owing to their many physiochemical similarities [1]. This renewable fuel is often synthesized by transesterifying bio-based oils with a light alcohol (methanol or ethanol) in the presence of an alkali catalyst (NaOH or KOH) [2]. Together with methyl/ethyl esters as the main product of transesterification process (also known as biodiesel), a significant amount of glycerol as the co-product is also generated. The soaring demand for biodiesel has increased global glycerol production as well, disturbing the well-established balance between its supply and demand. This in turn has spurred research into valorization of biodiesel–derived glycerol not only to avoid releasing glycerol-containing streams into the environment but also to improve the competitiveness of the biodiesel industry.

The biodiesel–derived glycerol can be effectively converted into various value-added chemicals like glycerol acetates (acetins) which can find a wide range of applications in food, fuel, pharmaceuticals, sanitary, and chemical industries [3]. Acetins, i.e., monoacetin, diacetin, and triacetin can be synthesized through glycerol esterification with acetic acid [3,4] and acetic anhydride [5,6] or transesterification with methyl/ethyl acetates [7]. It should be noted that acetins are often commercially produced by direct esterification of glycerol with acetic acid owing to the higher activity of acetic acid compared with methyl/ethyl esters as well as its lower price than acetic anhydride [3]. However, glycerol esterification with acetic acid is a thermodynamically-resistant and equilibrium-controlled chemical reaction [8]. Therefore, it is vital to use different strategies like using catalysts to propel forward this reversible reaction [9].

Different solid acid catalysts such as ion-exchange resin [5], mixed

---

* Corresponding authors at: Department of Mechanical Engineering of Agricultural Machinery, Faculty of Agricultural Engineering and Technology, College of Agriculture and Natural Resources, University of Tehran, Karaj, Iran (M. Aghbashlo).
E-mail addresses: maghbashlo@ut.ac.ir (M. Aghbashlo), maghbashlo@ut.ac.ir (M. Tabatabaei).

https://doi.org/10.1016/j.enconman.2018.03.054
Received 13 January 2018; Received in revised form 3 March 2018; Accepted 18 March 2018
0196-8904/

Nomenclature

$\mathbb{a}$	ash percentage (%)
b	environmental impact per exergy unit (mPts/GJ)
$\mathbb{B}$	specific environmental impact (mPts/GJ)
$\dot{\mathrm{B}}$	environmental impact rate (mPts/h)
c	cost per exergy unit (USD/GJ)
$\mathbb{c}$	carbon percentage (%)
C	specific heat capacity (kJ/kg K)
$\mathbb{C}$	specific cost (USD/kg)
$\dot{\mathrm{C}}$	cost rate (USD/h)
CRF	capital recovery factor (–)
ex	specific exergy (kJ/kg)
$\dot{Ex}$	exergy rate (kW)
f_b	exergoenvironmental factor (–)
f_c	exergoeconomic factor (–)
$\mathbb{h}$	hydrogen percentage (%)
H	annual working hours (h)
i	interest rate (%)
$\dot{m}$	mass flow rate (kg/s)
M	molar mass (kg/mol)
$\mathbb{n}$	nitrogen percentage (%)
$\dot{n}$	molar flow rate (mol/s)
N	reactor life time (year)
$\mathbb{o}$	oxygen percentage (%)
P	pressure (kPa)
R	universal gas constant (kJ/mol K)
r_b	relative environmental impact difference (–)
r_c	relative cost difference (–)
$\mathbb{s}$	sulfur percentage (%)
T	temperature (°C or K)
$\dot{\mathrm{W}}$	work rate (kW)
x	mass fraction (–)
X	acetic acid/glycerol molar ratio (–)
y	molar fraction (–)
$\dot{\mathrm{Y}}$	component-related environmental impact rate (mPts/h)
Z	investment cost (USD)
$\dot{\mathrm{Z}}$	component-related cost rate (USD/h)

Subscript

0	dead state
AA	acetic acid
BP	by-product
ch	chemical
D	destruction
DA	diacetin
e	exit
f	fuel
GL	glycerol
i	inlet
j	numerator
l	loss
MA	monoacetin
p	product
ph	physical
q	heat transfer
TA	triacetin
TOT	total
w	work
WT	water

Greeks

ε	standard chemical exergy value (kJ/mol)
ϕ	maintenance factor (–)

oxide catalysts [10], zirconia-based solid acid catalysts [11], heteropolyacids-supported on activated carbon [12], sulfated-activated carbon catalysts [13], fibrous mesoporous hybrid silica [14], zirconia-supported heteropolyacid acids [15], tungstophosphoric acids [16], magnetic solid acid catalysts [17], and bio-derived carbon catalysts [18] have been used to address this issue. However, the application of the above-mentioned catalysts often leads to the formation of undesirable products like acetol resulted from glycerol dehydration, negatively influencing the color and odor of the acetins evolved. In addition, the subsequent product purification and separation processes will be problematic issues in the presence of such products.

In order to address the above-mentioned issues, an easy-to-scale up continuous system was introduced and elaborated by Rastegari et al. [3]. Regardless of the promising experimental results yielded, emerging engineering processes and systems can only gain an opportunity to be commercialized if they are recognized as resource-efficient, cost-effective, and environmentally-benign approaches. Among the various methodologies introduced in the literature, exergy-based methods have been proven to be valuable tools for improving the thermodynamic, economic, and environmental performance of chemical processes.

Simply speaking, exergy is the maximum theoretical useful work obtainable from an energy system when it is brought into an equilibrium thermodynamically with the surroundings through reversible processes [19,20]. This concept can not only reveal real thermodynamic value of a material/energy flow but also measure its economic value and ecological wealth [21]. Using this unique tool, the location, magnitude, and causes of thermodynamic imperfections of engineering processes can be precisely determined [22]. These inefficiencies are caused by irreversibilities within the process, i.e., exergy destruction and exergy transfer to the environment, i.e., exergy loss. During the past few decades, there has been a great deal of research efforts exploring how and by how much engineering processes can be improved using the exergy concept [23–25]. However, exergy analysis only identifies, locates, and quantifies the thermodynamic inefficiencies [26]; it neither provides information on the economic rationality nor offers knowledge on the environmental consequences of engineering processes.

The design of cost-effective and environmentally-friendly engineering processes can be achieved by elaborated extensions of the exergy analysis viz. exergoeconomic and exergoenvironmental approaches, respectively [27]. These analyses could provide more informative results and yield additional insights that cannot be inferred from the conventional exergy analysis and economic/environmental accounting methods. Therefore, the costs and environmental impacts associated with the production processes can be systematically minimized by means of exergoeconomic and exergoenvironmental methods in order to address both energy and environmental issues. In the past few years, numerous attempts have been made to use these methods for analyzing and optimizing engineering processes from the thermodynamic, economic, and environmental viewpoints, simultaneously. For example, Akbulut et al. [28] experimentally and theoretically explored a vertical ground source heat pump-integrated wall cooling system from the exergoenvironmental and exergoeconomic viewpoints. Ahmadi Boyaghchi and Chavoshi [29] optimized a micro solar-geothermal combined cooling, heating, and power system integrated with flat plat collectors with water/copper oxide mixture as working fluid using exergy, exergoeconomic, and exergoenvironmental methods. Aghbashlo et al. [30] investigated the performance of a DI diesel engine