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Exergetic evaluation of renewable light olefins production from biomass via synthetic methanol

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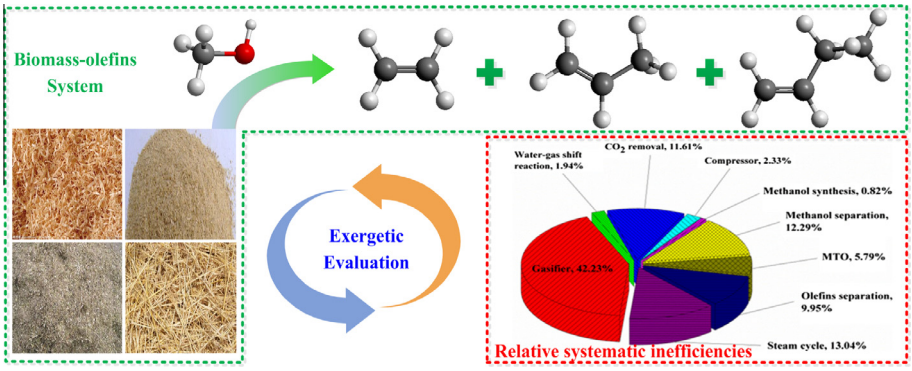
HIGHLIGHTS

- A two-step process for biomass–olefins production via synthetic methanol was simulated.
- The mass yield of the system was 0.248 kg light olefins kg^{-1} biomass.
- The system energetic and exergetic efficiencies were 54.66% and 47.65%, respectively.
- Biomass gasification, steam cycle and components separation units produced the major irreversibilities.
- Main efforts should be made on improvement of biomass gasification and energy integration processes.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, an exergetic evaluation was conducted on a two-step biomass-derived light olefins system established using ASPEN PLUS. This system linked methanol synthesis via entrained-flow gasification to a methanol-to-olefins (MTO) process. The mass yield of the system was 0.248 kg light olefins per kg biomass, which is relatively higher than the literature results. The energetic and exergetic efficiencies of this system were 54.66% and 47.65%, respectively. The results of an exergetic analysis indicate that the biomass gasification, steam cycle, methanol separation, CO_2 removal and olefins separation produce most of the system inefficiencies. By identifying the occurrence mechanism of the exergy losses, the potential for improvement can be obtained. A further increase of exergetic performance can be obtained from (1) improvement of gasification process via combining biomass torrefaction, and (2) enhancement of energy integration processes via heat network optimization and power generation from the produced steam.

1. Introduction

As the basic organic feedstock of the modern chemical industry, light olefins (ethylene, propylene and butene) are not only used as key monomers for synthetic polymers but also for synthesizing a wide range of chemicals such as epoxy ethane, benzene, styrene, propylene oxide, and isopropyl benzene [1,2]. Currently, light olefins are primarily produced through steam cracking of petrochemicals including naphtha, diesel and ethane [3]. With limited petrochemical resources and the associated serious environmental pollutions, developing alternative pathways for light olefins production has demanded increasing attention.

Methanol-to-olefins (MTO) technology has opened up a new way for alternative olefins production from diversified carbon feedstocks, ranging from natural gas over crude oil to coal [4]. Recently, a number of coal-to-methanol-to-olefin (CTO) projects

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Nomenclature

Abbreviations

MTO	methanol to olefins
WGS	water–gas shift reaction
O/B	oxygen/biomass ratio
S/B	steam/biomass ratio
MEA	monoethanolamine
HHV	higher heating value (kJ kg^{-1})
LHV	lower heating value (kJ kg^{-1})

Roman letters

E_x	exergy rate (MJ/kg light olefins)
T	temperature (K)
P	pressure (MPa)
Q	heat (kJ)
H	specific enthalpy (kJ kg^{-1})
S	specific entropy (kJ kg^{-1} K^{-1})
R	ideal gas constant (kJ mol^{-1} K^{-1})
m	mole fraction
z	mass fraction

Greek letters

β	ratio of chemical exergy to the lower heating value
η	efficiency (%)

Superscripts

Q	thermal energy input
ph	physical
ch	chemical

Subscripts

in	inlet
out	outlet
loss	losses
x	exergy
i	component i
0	reference state
H	hydrogen
O	oxygen
C	carbon

have been established and put into commercial operation in China [5]. Nevertheless, olefins production via synthetic methanol derived from natural gas or coal still cannot be conducive to lessening long-term reliance on fossil resources and greenhouse gas emissions. Fortunately, renewable carbon–neutral biomass resources can well compensate for such deficiency. Biomass is considered the mainstay in strategies to substitute fossil fuel as a raw feedstock for producing hydrogen, liquid fuels and other high-value chemicals. In recent years, renewable methanol synthesis via biomass gasification (bio-methanol) has been widely researched and developed into a mature technology [6–8]. As a result, a tandem biomass–olefins technique which combines bio-methanol synthesis and MTO can enable the renewable olefins production from lignocellulosic biomass. Though there exist only a few on-going researches, by far, focused on the biomass–olefins process, it is imperative to have knowledge on the performance evaluation and potential prediction of such a biomass–olefins process before industrial application. Furthermore, to exhaust its potential and enhance its competiveness with the fossil-based olefins, the biomass–olefins process ought to be as efficient and sustainable as possible. A preferred effective methodology for assessing energy process is exergetic analysis, which is able to provide the most natural criteria to develop process configuration and operating conditions for process improvement [9,10].

Contrast to energy which is always conserved (the 1st law of thermodynamics), exergy is never in balance for a real process (the 2nd law of thermodynamics). Exergetic analysis offers a unique sight to identify the useful part of energy and detect the process inefficiencies, which cannot be implemented by a traditional energetic analysis [11,12]. In the past few decades, exergetic analysis has been widely adopted to assess the performance of various biomass conversion processes [9–11,13,14]. To the best of the authors' knowledge, there is still no work published on the exergetic assessment of the biomass–olefins process. Thus, the present study is expected to fill this gap, in order to actively drive the potential excavation and performance optimization for biomass–olefins production.

First, the process involved in converting lignocellulosic biomass into light olefins via a two-step process is described in detail. Next, the methodology for the process simulation using ASPEN PLUS and exergetic evaluation is presented. Following, the modeling results including mass and energy balances as well as thermodynamic performance are assessed and then verified with the existing experimental or literature data. Subsequently, the thermodynamic imperfection for each unit/sub-process is fully identified and quantified. The causes of these exergy losses are then discussed separately. Finally, the improvement potential for the process with high inefficiencies is outlined, and the essential approaches for improving the process performance are discussed and proposed.

2. Process description

Fig. 1 demonstrates a simplified block diagram scheme of the biomass–olefins system. In this system, biomass feedstock is first disintegrated in an entrained-flow gasifier to produce syngas, which is then synthesized into methanol prior to the final conversion into light olefins.

2.1. Biomass gasification

As the most effective biomass conversion technology, biomass gasification is a partial oxidation process converting biomass into a high production of a gaseous mixture and small quantities of char and ash [15]. According to various hydrodynamics, several types of gasifiers including a fixed-bed gasifier, a fluidized-bed gasifier and an entrained-flow gasifier have been developed during the last couple of decades. In the present work, high-temperature entrained-flow gasification was employed due to its low emission rate, high carbon conversion rate, and high gasification efficiency. This method results in high-quality syngas with a high content of H_2 and CO and a very low amount of methane and tars [16]. Wheat-straw (from Jiangsu Province, China) was selected as the feedstock; its properties are summarized in Table 1. To meet the requirements of gasifier feeding, wheat-straw was ground to 150–250 μm before entering into the entrained-flow gasifier. On the other hand, the gasifier was operated autothermally, simplifying the system structure and minimizing the need for external energy inputs.

To enable methanol synthesis, gas cleaning and conditioning is of great significance for the crude syngas leaving the gasifier. Particulates and impurities that would poison the catalysts in the

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