

Integrated process for electrocatalytic conversion of glycerol to chemicals and catalytic conversion of corn stover to fuels



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ABSTRACT

This study presents two biomass conversion strategies: electrocatalytic glycerol-to-chemicals (eGTC) and catalytic corn stover-to-fuels (cCTF). The effect of process integration combining eGTC with cCTF on a commercial scale is investigated to improve energy efficiency and economics of the strategies. In the integrated process strategy, most of the heat requirements for eGTC are supplied by cCTF, and most of the hydrogen requirements for cCTF are provided by eGTC. Process integration leads to higher energy efficiency (27.6%) of integrated process strategy compared to the eGTC-only process (11.4%). The minimum selling price for the integrated process strategy is estimated to \$2.35/kg_{GLA} which can be more economically feasible than the eGTC-only process strategy (\$2.55/kg_{GLA}).

1. Introduction

Non-food biomass (the second and third generation biomass) can be used as feedstock for synthesis of fuels and commodity chemicals in a process that does not compete with food supply have been recent attention [1–8]. Bio-ethanol production using the second generation biomass (lignocellulose) is near to being commercially available but has still high feedstock cost due to its long cultivation period and large land usage. Processing the third generation biomass is relatively free from the problem of feedstock procurement (harvesting cycle is very short, and growth rate is very high) but still relatively costly due to a complicated process for recovering the suspended biomass derivatives [9,10]. Research is being conducted to identify process integration opportunities that use two or more different types of biomass to make biomass conversion commercially viable and overcome the limiting requirements of the individual processes [11,12]. The other research trend in the biomass conversion is product diversification to flexible response to changing market conditions [4,13,14]. The low crude oil prices have been lowering the profitability of biofuels production, and it moves the research direction to the simultaneous production of value-added chemicals as well as fuels from biomass. There have been a

number of economic feasibility studies of bio-based process co-producing fuels and chemicals on a commercial scale, showing the possibility of replacing petro-based process to bio-based process [1,2,4,13,15]. This study develops an integrated bio-based process to produce two different types of products (transportation fuels and chemicals) from two different types of biomass (as the second and third generation biomass) and investigates the effect of process integration.

The third generation biomass including micro- and macro-algae can be converted to biodiesel, one of the promising alternative transportation fuels [16,17]. Production capacity of biodiesel has been increasing rapidly in recent years, but it has still a market entry barrier for alternative transportation fuels due to its relatively high production cost [18]. To continue the viability of biodiesel by lowering the production cost, the effective utilization of glycerol as a major byproduct in the biodiesel production process has been viewed with increasing interest [19–22]. Glycerol can be converted to value-added chemicals based on the various conversion technologies such as oxidation, hydrogenolysis, and decomposition [23,24]. Oxidized glycerol derivatives, such as glyceric acid (GLA), glyceraldehyde (GAD), and hydroxypyruvic acid (HPA) can be used as monomers or as ingredients in the polymer and cosmetics industries, which have been shown remarkable

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Nomenclature

ACC	annualized capital cost, \$/y
AOC	annualized operating cost, \$/y
C ₅	hemicellulose
C ₆	cellulose
cCTF	catalytic corn stover-to-fuels
eGTC	electrocatalytic glycerol-to-chemicals
FCI	fixed capital investment, \$
FE	faradaic efficiency, %
FF	furfural
FFA	furfuryl alcohol
GAD	glyceraldehyde
GLA	glyceric acid

gly	glycerol feed concentration, M
GVL	γ -valerolactone
HPA	hydroxypyruvic acid
JFA	jet fuel range alkenes
LA	levulinic acid
MSP	minimum selling price, \$/kg _{GLA}
MW _e	megawatt-equivalent, MW
SA	sulfuric acid
TC	total cost, \$/y
TCI	total capital investment, \$
TOF	turnover frequency, h ⁻¹
V _A	anode voltage, V
WWT	wastewater treatment

market growth [25,26].

Electrocatalytic oxidation can be used to produce high yields of GLA, GAD, and HPA; the process use only water as a stoichiometric chemical oxidant and commercial 20 wt% Pt/C as a catalyst [26]. The products can be recovered from dilute aqueous solution by vapor-liquid equilibrium distillation. However, potential challenges for further development of the process are (1) large amounts of heat requirements for the downstream separations necessary to recover the oxidized chemicals from dilute aqueous solution and (2) the effective utilization of hydrogen, a valuable byproduct generated at the cathode side, that could be used for other hydrogenation reactions or generation of heat and electricity. Accordingly, the electrocatalytic oxidation technology should be explored to be integrated into a process with other exothermic hydrogenation technologies to overcome bottlenecks between the two technologies.

Lignocellulose (including corn stover, sugarcane bagasse, straw) as the second generation biomass is a potential renewable source to produce alternative transportation fuels and commodity chemicals [13,27–33]. Lignocellulosic biofuels, such as bioethanol, biobutanol, and biogasoline, can be produced through three different conversion technologies: biochemical, thermochemical, and catalytic [15,29]. Catalytic treatment of corn stover can produce jet fuel range alkenes (JFA; i.e., C₈ to C₂₀), which can be targeted for gasoline or jet fuel application [1,4,15,34–37]. Catalytic JFA-production technology applies chemical hydrolysis and dehydration of corn stover to platform

chemicals (levulinic acid (LA) and furfural (FF)) obtained by treatment of corn stover, then hydrogenates them catalytically to γ -valerolactone (GVL) intermediate and ultimately to JFA [38–40]. One of the key impediments to commercialization of catalytic JFA technology is that GVL cannot yet be produced inexpensively. cCTF can convert corn stover to LA and FF at high yields by using LA- and FF-derived GVL as a solvent, then upgrading the platform chemicals to GVL over three bi-metallic catalysts (Pt₃Sn/SiO₂, Amberlyst 70, RuSn₄/C) [1]. The process of using GVL solvent could reduce the cost of GVL production by simplifying the steps involved in its purification. However, commercialization of cCTF requires (1) efficient utilization of heat exhausted from exothermic reactions (i.e., hydrolysis and dehydration of corn stover; hydrogenation of FF and LA, and (2) high-pressure H₂ for GVL production from LA.

The requirements and wastes of eGTC complement those of cCTF. Therefore, there is an expectation that the economic efficiency of each process can be improved by integrating them. Such integration would reduce material costs by using H₂ exhaust from eGTC as an input to cCTF, and also reduce utility costs by transferring waste heat from cCTF to derive eGTC. This integration would reduce the sensitivity of the integrated process to market prices of biomass feedstocks and bio-based products, and thereby suppress cost increases in the integrated process.

This study presents a schematic framework for economic feasibility analysis of the integrated eGTC and cCTF process. The framework follows three steps: process synthesis, energy analysis, and economic

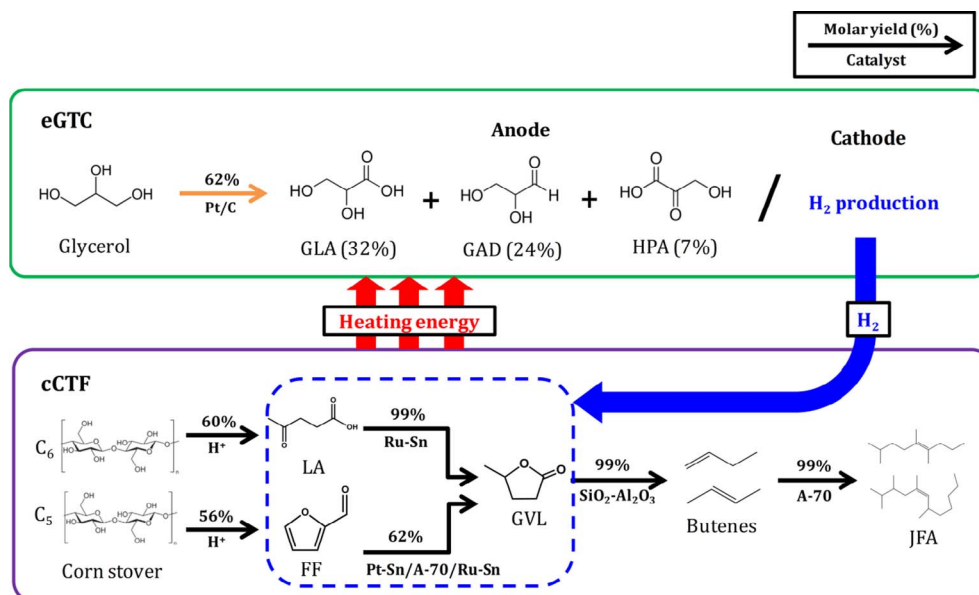


Fig. 1. Reaction schematic view of the eGTC and cCTF in this study.

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