

TECHNO ECONOMIC FEASIBILITY STUDY FOR CATALYTIC BUTENE OLIGOMERS PRODUCTION FROM LIGNOCELLULOSIC BIOMASS USING 2-SEC-BUTYLPHENOL SOLVENTS

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ABSTRACT

Lignocellulosic biomass is one of the most promising resources for production of transportation fuels. Butene oligomers, which can be used as a gasoline range fuel, can be derived from lignocellulosic biomass. This work performs a techno economic feasibility study for a strategy for catalytic butene oligomers (BO) production from lignocellulosic biomass using 2-sec-butylphenol (SBP) solvents. Our strategy includes the pretreatment step to obtain cellulose and hemicellulose separately from lignocellulosic biomass. After pretreatment, the cellulose fraction can be converted to levulinic acid (LA) by monophasic reaction, while the hemicellulose fraction can be converted to LA by biphasic reaction followed by hydrogenation. The LA is then converted to BO via γ -valerolactone (GVL) and butene production. Moreover, this study designs separation subsystems not only to fit optimized feed concentration for catalytic reactions but also to recycle SBP solvents for the reactions. To minimize energy requirements of the process, a heat exchanger network including heat integration between process streams is designed, and thereby the energy requirements can be satisfied by combustion of biomass residues (lignin). Our strategy has advantages: (1) high biomass-to-fuels yield (37.1%) (2) high biomass-derived intermediate recovery (72-99%) (3) high SBP recovery (99%). Our techno economic evaluation reports that the proposed strategy leads to a minimum selling price (MSP) of \$4.38 per gallon of gasoline equivalent (GGE) for butene oligomers using a corn stover feedstock. This study also performs sensitivity analyses for identifying the impacts of four key economic parameters on the MSP and the analyses show that the MSP can be decrease to \$3.71 GGE⁻¹ when using best possible parameters.

INTRODUCTION

Lignocellulosic biomass is a promising feedstock for biofuel production and it comprises of cellulose (C₆), hemicellulose (C₅) and lignin. [1]. The C₆ and C₅ fractions of lignocellulosic biomass can be converted to biofuels through catalytic route [2-4], while the lignin is used for heat and power production through combustion [5]. Sen et al. [6-8] showed strategies for production of the liquid hydrocarbon fuel (BO)

from the catalytic conversion of the C₆ fraction of lignocellulosic biomass. The major drawback in these strategies is a low overall biomass-to fuel yield, because the fuels are produced from the C₆ fraction of lignocellulosic biomass and the C₅ is used for supplying heat and electricity in the process. To overcome this drawback, this strategy converts C₅ components of the lignocellulosic biomass to fuels, thereby increasing the biomass-to-fuels yields of the overall process. According to Gürbüz et al. [9], C₅ fraction of lignocellulosic biomass can be converted into furfural (FF) and LA by using biphasic reactors with an 2-sec-butylphenol (SBP) solvent. The LA can be converted to GVL and BO [10]. This study shows a strategy for the process synthesis for catalytic conversion of the C₆ and C₅ fractions of the lignocellulosic biomass to liquid hydrocarbon fuels and performs a techno economic evaluation. This strategy is mainly based on (1) the catalytic pretreatment subsystem (2) the catalytic C₆-to-fuels subsystems including the separation subsystems (3) the catalytic C₅-to-fuels subsystems including the separation subsystems.

NOMENCLATURE

C ₆	Cellulose
C ₅	Hemicellulose
SBP [†]	2-sec-butylphenol
LA [†]	Levulinic acid
GVL [†]	γ -valerolactone
BO [†]	Butene oligomers
FA [†]	Formic acid
FF [†]	Furfural
FFA [†]	Furfuryl alcohol
SA [†]	Sulfuric acid
NaCl [†]	Sodium chloride
H ₂ [†]	Hydrogen
Ru [†]	Ruthenium
Sn [†]	Tin
Si [†]	Silicon
O [†]	Oxygen
Al [†]	Aluminium
Cu [†]	Copper
Mg [†]	Magnesium
Mt [†]	Metric tonne
HEN [†]	Heat exchanger network
GGE [†]	Gallon of gasoline equivalent
MSP [†] [\$ /GGE]	Minimum selling price

[†] Developed abbreviation

[†] Obtained abbreviation [6], [9], [11], [12]

TECHNOLOGY OVERVIEW

This strategy combined two catalytic conversion methods of components of biomass (C_6 and C_5) to **liquid hydrocarbon fuel (BO)**. This strategy used an integrated method developed by Sen et al. [25] for the conversion of C_6 to BO and developed an integrated method for the conversion of C_5 to BO. The C_6 -to-BO conversion strategy [6] includes three catalytic conversion subsystems for the (1) hydrolysis and dehydration of C_6 to LA [13], (2) LA reduction to GVL [14], and (3) conversion of GVL to BO [10]. Serrano-Ruiz et al. [13] reported that the C_6 fraction of biomass can be converted to LA and formic acid (FA) with 55 mol% yield in a batch reactor at 473 K and 16 bar, using a water solvent with 0.5 M SA catalyst (Reaction 1 in Figure 1). Alonso et al. [14] proposed a biphasic separation system that extracts intermediate chemical from aqueous phase by using SBP solvent. Most of the LA partitions into the organic (SBP) phase whereas some of FA (29%) partitions in the organic (SBP) phase. The LA can then be converted to GVL in SBP solution with 99 mol% yield at 493 K and 36 bar over RuSn (1:4)/C catalyst (Reaction 2 in Figure 1) [14]. Finally, Bond et al. [10] presented that a solution of GVL with water can be converted to BO with 99 mol% yield over a double-catalyst bed system (SiO_2/Al_2O_3 (648 K) and Amberlyst-70 (443 K)) at 36 bar (Reactions 1-2 in Figure 2).

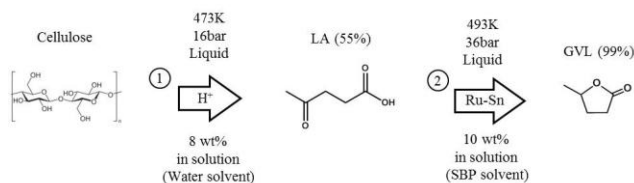


Figure 1 Conversion of C_6 to GVL (adapted from [6])

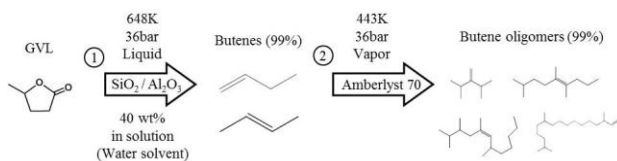


Figure 2 Conversion of GVL to BO (adapted from [6])

The C_5 -to-BO conversion strategy includes five catalytic conversion subsystems for the (1) biphasic hydrolysis of xylose to FF [9], (2) conversion of FF to furfuryl alcohol (FFA) [12], (3) biphasic conversion of FFA to LA [9], (4) LA reduction to GVL [14], and (5) conversion of GVL to BO [10]. Gürbüz et al. [9] presented that the C_5 -derived xylose can be converted to FF with a 78 mol% yield in a biphasic reactor system at 443K and 1bar, using organic (SBP) and aqueous (water) solvents with 0.1M hydrochloric acid (HCl) catalyst and saturated sodium chloride (NaCl) (Reaction 1 in Figure 3). The FF (90%) partitioned in the organic (SBP) phase when the aqueous (water) phase is saturated with NaCl. After the biphasic reaction, SBP is separated from the FF by distillation. Nagaraja et al. [12]

presented that the FF stream can be converted to FFA with 96 mol% yield over a Cu-MgO catalyst in a fixed bed reactor at 453K and 1bar in a H_2 -rich condition (H_2 : FF molar ratio = 2.5:1) (Reaction 2 in Figure 3). Gürbüz et al. [9] also showed a biphasic reactor system wherein FFA can be converted to LA with a 67 mol% yield at 398K and 1bar, using organic (SBP) and aqueous (water) solvents with 1M SA catalyst (Reaction 3 in Figure 3). They proved that high concentrations of FFA in reactive aqueous solution encourage side reactions, thus keeping low concentrations of FFA in aqueous solution is necessary for high LA yields. When using an organic solvent (SBP), FFA concentration significantly decrease in biphasic reactor and that results in high yield of LA by decreasing side reactions. Finally, the LA can be reduced to GVL (Reaction 2 in Figure 1) and then converted to a mixture of BO based on the above mentioned reactions (Reactions 1-2 in Figure 2).

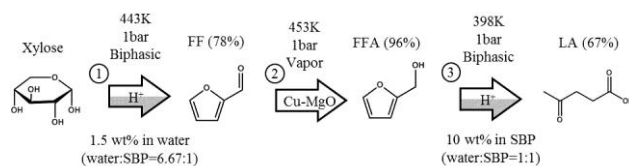


Figure 3 Conversion of xylose to GVL (adapted from [9, 12])

DESIGN BASIS AND ASSUMPTION

This study develops a simulation model for our strategy which includes seventeen processing steps using the ASPEN Plus Process Simulator [15]. The equipment costs of twelve steps (LA production of C_6 conversion, SA recovery of C_6 conversion, GVL production of C_6 conversion, SBP recovery of C_6 conversion, FF production of C_5 conversion, FFA production of C_5 conversion, LA production of C_5 conversion, GVL production of C_5 conversion, SBP recovery 1 of C_5 conversion, SBP recovery 2 of C_5 conversion, butene production, and butene oligomerization) are assumed using the ASPEN Process Economic Analyzer [16], whereas the equipment costs of the remaining steps (biomass handling, pretreatment, wastewater treatment, boiler/ turbogenerator, and storage) are calculated using an exponential scaling expression based on the the NREL's design [17, 18]. Also, the equipment and utility costs of the HEN are calculated using the ASPEN Energy Analyzer [19]. Our strategy adopts same feedstock, processing rate (2000 metric tonnes (Mt) d^{-1}) and economic parameters of NREL's design [17, 18].

PROCESS DEVELOPMENT

This study developed an integrated process based on the aforementioned technologies for production of liquid hydrocarbon fuels (BO) from C_6 and C_5 fractions of lignocellulosic biomass. The integrated fuel production process includes seventeen steps: biomass handling, pretreatment, wastewater treatment, boiler/turbogenerator, storage, LA production of C_6 conversion, SA recovery of C_6 conversion, GVL production of C_6 conversion, SBP recovery of C_6

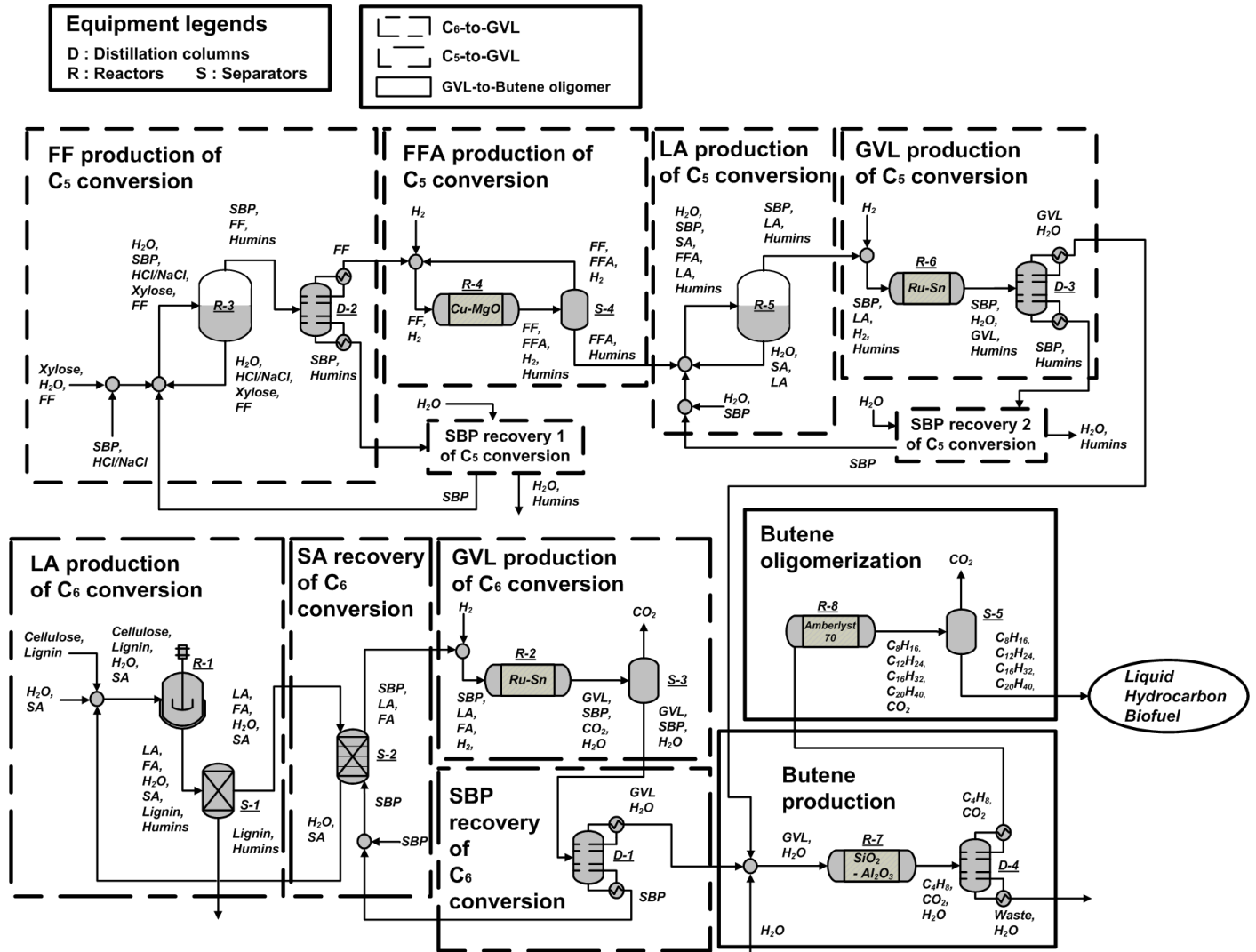


Figure 4 C₅ and C₆ conversion subprocess

conversion, FF production of C₅ conversion, FFA production of C₅ conversion, LA production of C₅ conversion, GVL production of C₅ conversion, SBP recovery 1 of C₅ conversion, SBP recovery 2 of C₅ conversion, butene production, and butene oligomerization.

Corn stover is physically treated to reduce size in biomass handling step, then chemically treated using 0.5 M SA in pretreatment step for separating the C₅ from the C₆ and lignin [17]. Most of the C₅ is converted to soluble xylose (92.5 mol%) and FF (5 mol%) in the pretreatment step, then filtered for separation of solid and liquid fractions. The solid fraction (containing C₆ and lignin) is sent to C₆-to-GVL conversion subprocess while the liquid fraction (containing xylose, SA and water) is neutralized and sent to C₅-to-GVL conversion subprocess.

The C₆-to-GVL conversion subprocess includes four steps, as shown in Figure 4: LA production of C₆ conversion, SA recovery of C₆ conversion, GVL production of C₆ conversion, and SBP recovery of C₆ conversion. After the LA production of

C₆ conversion (R-1 in Figure 4; Reaction 1 in Figure 1), liquid mixture (containing LA, FA, SA, and water) is separated from insoluble materials (lignin and humins) by liquid-solid separator (S-1 in Figure 4). Then SA solution is removed from the liquid mixture by extraction using SBP at 453 K and 16 bar with a SBP to feed mass ratio of 4.4. After 6 extraction stages (S-2 in Figure 4), LA (100%), FA (29%), and recycled GVL (97%) are recovered in the organic (SBP) phase, while the remaining materials in the SA solution are recycled back to the R-1. After GVL production (R-2 in Figure 4; Reaction 2 in Figure 1), 80% of the CO₂ is separated by a flash tank at 380 K (S-3 in Figure 4), and most of SBP (99.8%) is recovered at the bottom of a 33-stage distillation column (D-1 in Figure 4) at 512 K and 1 bar, then it can be reused in the SA recovery step (S-2 in Figure 4). Through GVL-SBP distillation, 95 wt% of GVL is also obtained at the top of the distillation column (D-1 in Figure 4) at 347 K and 1 bar. The distilled GVL is converted to butene oligomers in two catalyst bed reactors (R-7 and R-8 in Figure 4; Reactions 1-2 in Figure 4). The reactors are connected with a 20-stage distillation column (D-4 in Figure 4)

to adjust the feed compositions of R-6 reactor. Most of the butene (99.9%) is obtained at the top of distillation column (D-4 in Figure 4) at 378K and 1bar. Finally, a vapor stream (94.9%) of CO₂ is separated from the BO (C₈H₁₆, C₁₂H₂₄, C₁₆H₃₂, C₂₀H₄₀) and the BO are condensed to form a liquid fuel (S-5 in Figure 4).

The C₅-to-GVL conversion subprocess includes six steps, as shown in Figure 4: FF production of C₅ conversion, FFA production of C₅ conversion, LA production of C₅ conversion, GVL production of C₅ conversion, and SBP recovery 1 of C₅ conversion, SBP recovery 2 of C₅ conversion. After pretreatment, xylose is converted to FF in a biphasic reactor (R-3 in Figure 4; Reaction 1 in Figure 3), which leads to separate aqueous streams and organic (SBP). The organic (SBP) stream (including FF and humins) is sent to a distillation column (D-2 in Figure 4) to separate FF from SBP solution. High purity FF (99 wt%) is obtained at the top of a 15-stage distillation column (D-2 in Figure 4) at 435 K and 1 bar. Following distillation, distilled FF is converted to FFA in a fixed bed reactor (R-4 in Figure 4; Reaction 2 in Figure 3) under a H₂-rich condition and then most of H₂ is separated by a flash tank at 393 K (S-4 in Figure 4). The FFA-rich mixture is sent to produce LA in a biphasic (SBP/water) reactor (R-5 in Figure 4; Reaction 3 in Figure 3). After conversion, the organic (SBP) stream containing LA is separated from the aqueous stream containing SA, and the aqueous stream can be reused in the biphasic reactor (R-5 in Figure 4). LA in organic solution is converted to GVL in a H₂-rich condition (R-6 in Figure 4; Reaction 2 in Figure 1). After GVL/SBP distillation, high purity GVL (99.7 wt%) is also obtained at the top of the 39-stage distillation column (D-3 in Figure 4) at 459 K and 1 bar and the distilled GVL is converted to BO as in the previous steps (R-7, R-8, D-4, S-5 in Figure 4). Our process requires the large SBP solvent to extract biomass-derived intermediates in biphasic reactor systems, thus the recovery and reuse of SBP is necessary. Also, humins can be used for heat and electricity supply. Therefore, this study designs separation subsystems for recovery of SBP and humins (SBP recovery 1 of C₅ conversion and SBP recovery 2 of C₅ conversion). Most of SBP (99%) is recovered by the separation subsystems and recycled to biphasic reactors (R-3, R-5 in Figure 4). Separated humins are combusted to produce high-pressure (HP) steam in a boiler. A part of the steam is used to satisfy the heating requirements for the process, while the remaining steam is used for generation of electricity in a turbogenerator unit [17]. The overall biomass to fuels (BO) molar yield of our process design is 37.1%.

HEAT INTEGRATION

The energy content of corn stover is 358 MW which is composed of C₆ and C₅ (220 MW, 61.4% of corn stover), lignin (98 MW, 27.4% of corn stover) and other components (40 MW, 11.2% of corn stover) when the base capacity is 2000 tons per day. In our strategy, 285 MW of heat is required for integrated process, and the energy content of liquid hydrocarbon fuel is 118 MW, which is 53.6% of the energy content of C₆ and C₅. Our strategy can produce 158 MW of heat from combustion of biomass residues (222MW), when the efficiency of boiler is 71%

[17], which cannot satisfy the total heating requirements (289 MW). Thus, this study performs heat integration for reducing the energy requirements with design of a HEN consists of 56 heat exchangers. After heat integration, 191 MW of heat are recovered, and the heating requirements for our process are reduced to 98MW.

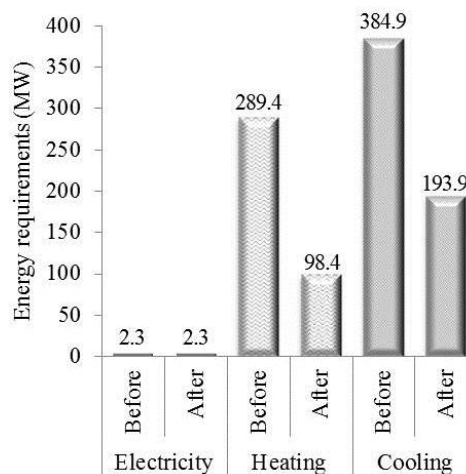


Figure 5 Energy requirements of integrated process

The energy flow diagram in Figure 6 presents the energy efficiency (the ratio of the energy output (fuels and electricity) to energy input (biomass feedstock)). In our process, 118MW of liquid fuels and 23MW of excess electricity are produced from biomass (358MW), thus the energy efficiency for our process is 39.4%.

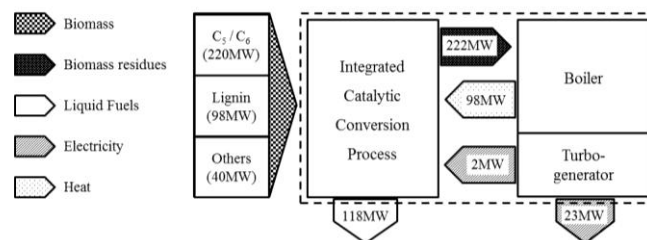


Figure 6 Energy flow diagram

ECONOMIC EVALUATION

The annualized capital and operating costs of all steps of our strategy are shown in Table 1. The total annualized capital costs are calculated based on the total installed equipment cost. The total installed equipment cost is converted to the total project investment which is sum of other direct costs and indirect costs. Then, the total project investment is annualized by using the capital charge rate which is correlated with the capital investment. The total annualized capital cost for our strategy is estimated to be \$44.3 million yr⁻¹ and the boiler/turbogenerator is the largest component of total annualized capital cost (27%). The total operating cost of our strategy is \$87.0 million yr⁻¹, and the feedstock costs including harvesting, transportation, and storage costs [11] are the most significant component of the total operating cost (52%). The

second largest component is material costs (H_2 , HCl , $NaCl$, SA , lime and SBP , $\$19.6$ million yr^{-1}), and remaining operating costs are other operating costs ($\$12.1$ million yr^{-1}) and fixed operating costs (e.g., labor, overhead, insurance and maintenance costs, $\$10.1$ million yr^{-1}). The total production cost (the sum of annualized capital and operating costs, for our strategy) is $\$131.3$ million yr^{-1} .

Table 1 Annualized capital and operating costs ($\$$ million yr^{-1}).

C : Capital cost (Annualized)		
O : Operating cost		
Components	C	O
<i>Process steps</i>		
Pretreatment	9.2	5.0 (3.3/1.7) ^a
Monophasic/biphasic* LA production	5.0/1.7*	2.5 (2.5/0) ^a / 6.9* (6.9/0) ^a
GVL production	4.0	13.0 (5.8/7.2) ^a
SA recovery	1.3	
GVL recovery		
SBP recovery	3.5	
Butene oligomers production	3.6	
Boiler/turbogenerator	12.0	1.1 (0/1.1) ^a
Other processing steps	3.9	3.1 (1.0/2.1) ^a
<i>Fixed operating costs</i>		10.1
<i>Feedstock cost</i>		45.2
<i>Total capital/operating cost</i>	44.3	87.0
<i>Total cost</i>	131.3	

^a (Material cost / Other operating cost)

- Material cost : H_2 , HCl , $NaCl$, SA , lime and SBP
- Other operating cost : catalyst regeneration, waste disposal, cooling water

* Biphasic LA production step includes FF production of C_5 conversion, FFA production of C_5 conversion and LA production of C_5 conversion.

A minimum selling price (MSP) of liquid hydrocarbon fuels are calculated using economic parameters and discounted cash flow analysis in the NREL's design [18]. The unit of MSP is gallon of gasoline equivalent (GGE). The total annualized cost for our strategy is $\$131.3$ million yr^{-1} , and the MSP is $\$4.38$ GGE^{-1} . The electricity credit obtained in our strategy is $\$0.40$ GGE^{-1} , which is 8.0% of the overall cost of liquid hydrocarbon fuels

($\$4.78$ GGE^{-1}) that is sum of MSP of liquid hydrocarbon fuels and electricity credit. This study performed sensitivity analyses to identify the impacts of four key economic parameters (discount rate (decreasing from 10% to 6.74%) [1, 4, 20], H_2 price (decreasing from $\$2.0$ kg^{-1} to $\$1.1$ kg^{-1}) [21], tax rate (decreasing from 35% to 13%) [22], and electricity price (increasing from $\$0.0572$ kWh^{-1} to $\$0.0639$ kWh^{-1}) [23]) on the MSP of liquid hydrocarbon fuels for our strategy. The results are shown in Figure 7. The MSP is decreased by $\$0.35$ GGE^{-1} when the discount rate decreased to 6.74% from 10%. When the hydrogen price and tax rate are decreased to $\$1.1$ kg^{-1} and 13%, the MSPs are decreased by $\$0.15$ GGE^{-1} and $\$0.12$ GGE^{-1} , respectively. The MSP is decreased by $\$0.05$ GGE^{-1} when the electricity price is increased to $\$0.0639$ kWh^{-1} . This analysis shows that the discount rate has the largest impact on the MSP and the MSP can decrease by $\$0.67$ GGE^{-1} to $\$3.71$ GGE^{-1} when all parameters are adjusted simultaneously.

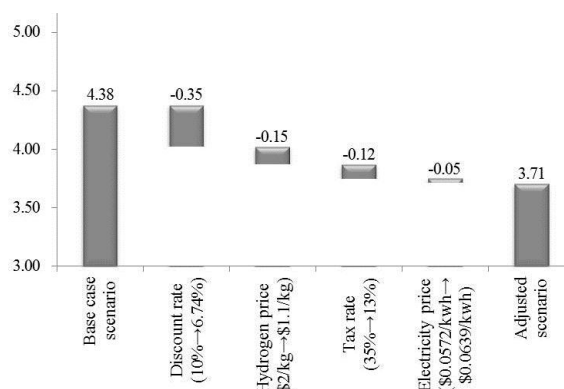


Figure 7 Impact of adjusting the key economic parameters ($\$$ GGE^{-1})

CONCLUSION

This study developed a strategy for the production of liquid hydrocarbon fuels (BO) from C_6 and C_5 based on catalytic conversion technologies using SBP solvent. This study presented that our strategy has high biomass to fuels molar yield (37.1%) but requires effective separation subsystems to recycle solvents (SBP) with effective HEN design. The separation subsystems with HEN design can recycle 99% of the SBP , and the total heating requirements are reduced to 98MW. As a result, the total energy requirements can be satisfied by combustion of biomass residues. In our strategy, 53.6% of the energy contents of C_6 and C_5 fractions of biomass can be converted to liquid hydrocarbon fuels. This study showed that when $2,000$ Mt d^{-1} of corn stover is processed and the existing economic parameters are used, the MSP of fuels is $\$4.38$ GGE^{-1} , which can be more decreased to $\$3.71$ GGE^{-1} using the best possible parameters.

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