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Techno-economic and uncertainty analysis of fast pyrolysis and gasification for biofuel production

Boyan Li
Iowa State University

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Techno-economic and uncertainty analysis of fast pyrolysis and gasification for biofuel production

by

Boyan Li

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Mark Wright, Major Professor
Robert Brown
Max Morris

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ABSTRACT

This thesis consists of uncertainty and techno-economic studies of two different biofuels production pathways (catalytic pyrolysis and gasification). The objective of this paper is to obtain a side-by-side techno-economic comparison of *in situ* and *ex situ* catalytic pyrolysis, and gasification state-of-technology and target scenarios that addresses both sensitivity and uncertainty analysis in the comparison of these four technologies.

Two journal papers have been published in Bioresource Technology and Energy Technology as the result of this study: “Techno-economic and uncertainty analysis of *in situ* and *ex situ* fast pyrolysis for biofuel production” and “Understanding uncertainty of transportation fuel production via biomass gasification and mixed alcohol synthesis”.

Uncertainty analysis shows that *in situ* catalytic pyrolysis is expected to have a similar minimum fuel-selling price (MFSP) with *ex situ* catalytic pyrolysis, $4.2 per gallon and $4.27 per gallon respectively. However, *in situ* catalytic pyrolysis tends to have greater techno-economic risk compared to the *ex situ* catalytic pyrolysis scenario. The state-of-technology gasification scenario, with a MFSP of $7.02 per gallon, is expected to have a significantly higher MFSP compared to the other three scenarios (*in situ, ex situ* and target gasification). The target gasification scenario yields a MFSP of $4.33 per gallon, which is similar to the catalytic pyrolysis scenarios. However, the economic risk associated with the target gasification scenario is significantly lower than the pyrolysis scenarios.

CHAPTER 1. GENERAL INTRODUCTION

Introduction

Since the first industrial revolution in the 18th century, fossil fuels have rapidly become one of the primary energy sources for human society. The Energy Information Administration (EIA) estimates that U.S. primary sources of energy consumption in 2014 reached 98.5 Quadrillion Btu. Of which 78% of the sources of energy accounts for fossil fuels which can be further separated to 34% petroleum, 27% natural gas, and 17% coal [1]. The fact that U.S. energy system is heavily dependent on fossil fuels makes the energy system vulnerable to any fluctuations in the global energy market. Therefore, the improvement of the current energy system and the development of an alternative energy system provide a chance to further enhance national security [2, 3]. Furthermore, fossil fuels have been a dominant source of U.S. energy consumption since 1950 making it a primary contributor for the greenhouse gas emission and global warming [1, 4]. If unchecked, the atmospheric CO_2 levels will eventually reach a critical value of 550 ppm within the century causing the early arrival of the next ice age [5, 6]. Thus a new energy structure is needed for the environmental concern. Moreover, the recent fluctuation of the gasoline and diesel fuel price reveals once again the uncertainty and volatility associated with fossil fuels. This event led to an increasing focus in developing alternative energy sources to ensure the economic stability. Among all the current renewable energy (biomass energy, hydro power, geothermal energy, solar energy, wind energy, etc.), biomass energy is the only energy resource having the potential to become a fossil fuel alternative, since it can produce fuels, chemicals, alternatives and energy [7]. Additionally, biomass is an environmentally friendly energy resource due to its zero net CO_2 emission in the carbon circulation [8, 9]. Furthermore, biomass energy also does not have the dependency on natural reservations such as petroleum or coal, it can utilize local agricultural products as feedstock, which considerably reduces the energy dependence, thereby benefitting national security [10]. In conclusion, biomass energy shows the greatest potential to improve environmental sustainability, economic stability, and national security [3, 11-13].

The annual use of 36 billion gallons of biofuels has to be achieved by 2022 according to the revised Renewable Fuel Standard (RFS2) announced by the US Environmental Protection Agency (EPA) [14, 15]. However, only bioethanol refinery plants have been widely and successfully used on commercial scales so far. In order to reach the ambitious goal set by EPA, a wide variety of biorenewable pathways, such as fast pyrolysis, gasification, fermentation, hydrothermal liquefaction must be investigated. Lots of efforts have been put into the technological improvement of these biorenewable pathways in recent decades [16]. With the continual development of biorenewable technology, cost analysis should be frequently updated, in order to provide a timely and accurate feedback on biorenewable development.

The main purpose of this study is to provide an up-to-date techno-economic analysis across multiple biorenewable pathways with the consideration of uncertainty. A side-by-side comparison regarding minimum fuel-selling price (MFSP) with mean and standard deviation for multiple scenarios is provided. An innovative sensitivity analysis is conducted to present the significance level for each key parameter among the different scenarios.

Background

There are a variety of pathways to convert biomass into desirable energy forms. Thermal conversion of biomass is one of the promising pathways which produce heat, chemicals and liquid form of fuels. By differentiating the quantity of oxygen, the process time and temperature, thermal conversion can be categorized into few types, such as combustion, pyrolysis, and gasification. In this study, catalytic pyrolysis and gasification are employed due to their technical maturity for bio-fuel production.

Pyrolysis

As one of the most ancient biorenewable technological pathway, pyrolysis has been used for biochar production for thousands of years [17]. Obviously, those ancient methods are detrimental to the environment, hence cannot be employed today. With the technological improvement, modern pyrolysis process is able to capture and utilize those once useless volatile gases to convert them into bio-oil and syngas [18, 19]. There are three types of biomass pyrolysis pathways and they are categorized as slow, intermediate and fast pyrolysis. Slow pyrolysis, set at relative low temperatures of around 250 ℃ with a residence time up to few days, is widely used for bio-char production, whereas intermediate and fast pyrolysis are heavily employed by bio-oil refineries [20]. For the past 30 years, fast pyrolysis which employs a quick thermochemical process operating around 500^{0}C in the absence of oxygen for less than 2 seconds has received increasing attention [21]. Figure 1 shows the principles of fast pyrolysis process. In modern fast pyrolysis process, in order to have a reaction in such short amount of time, the biomass feedstock has to be cut and grinded to a size of 2mm and dried until the moisture content is below 30 wt. % (usually around 12 wt. %) [22]. Since the typical biomass has a moisture content of 50-60 wt. %, some biomass, such as microalgae, has 80-90 wt. % of water contents, extra power input is required in the drying and preparation process [23]. With the present of catalysts (such as zeolite ZSM-5) during or right after the pyrolysis process, the quality and quantity of the bio-oil produced by the fast pyrolysis is then improved [24-26]. A pyrolysis vapor quench is employed to separate and condense the vapor from non-condensable gases. The condensed liquid stream is further separated into aqueous (mostly water) and organic fractions. The organic liquid stream is then deoxygenated and saturated in a hydrotreater for further upgrading [27]. After that, the targeted product, such as gasoline and diesel, can be separated according to their different boiling ranges. During co-generation process, electricity can be generated from the process heat [28].

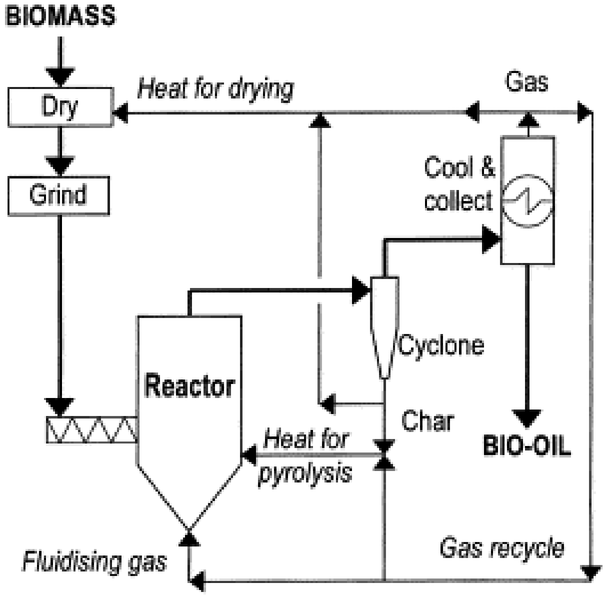

Figure 1 Fast pyrolysis process principles [29].

There are two subcategories of pyrolysis frequently discussed in literatures: *in situ* and *ex situ [30-35]*. As shown in figure 2, the *in situ* configuration places the fast pyrolysis and catalytic vapor upgrading within the same reactor, whereas the *ex situ* configuration uses a separate catalytic vapor phase upgrading reactor system after the non-catalytic fast pyrolysis reactor. Due to the relatively simple configuration, the initial capital cost for *in situ* is likely to be lower than *ex situ*. Since the fast pyrolysis and catalytic vapor upgrading happens in the same reactor, a more robust reactor for *in situ* scenario is required. By separating the catalyst with fast pyrolysis process, *ex situ* vapor phase upgrading reactor does not limit the size associated with biomass feed as *in situ* does [36]. Furthermore, in *ex situ* configuration, the catalyst is separated from the fast pyrolysis reactor, reducing the chance for catalyst contacting with solid contents, such as biomass, char and ash. This prevents the coking on the catalyst thereby considerably increasing the catalyst life [30, 37]. The liquid fraction yield for *in situ* and *ex situ* shows no significant difference, whereas the aromatics and phenols content, which can be further upgraded to transportation fuels, in *in situ* scenario is higher.

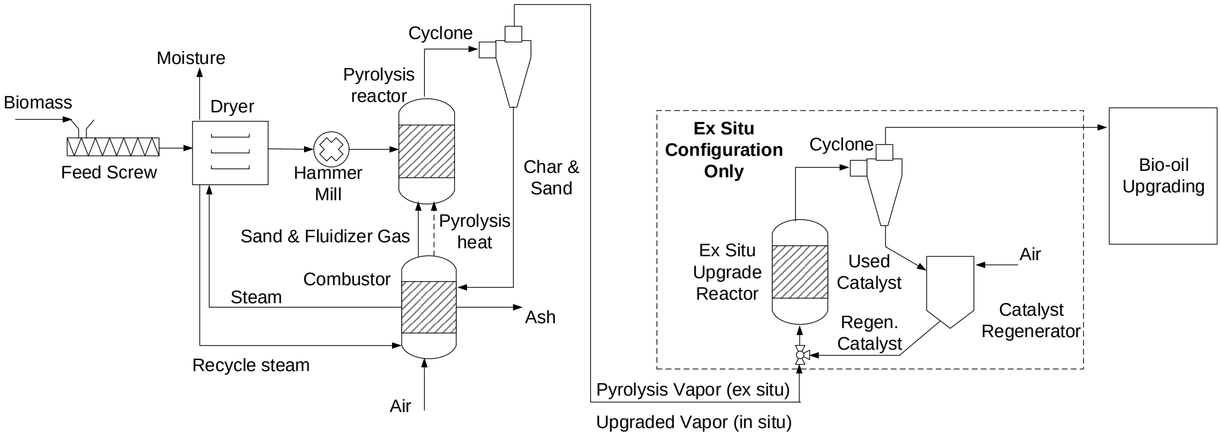

Figure 2 Difference between *in situ* and *ex situ* catalytic pyrolysis.

Heat and electrical power can be generated by a Combined Heat and Power (CHP) system. Process heat recovered by a CHP system can be used to remove moisture content in biomass or power an electricity generator. The installation of a CHP system is flexible and can be designed on a scale ranging from 50kWe to 15MWe [38]. Therefore, the cost can vary significantly depending on the design. In general, an efficient CHP system can achieve primary energy savings of approximately 40% [39].

Gasification

Gasification is a thermochemical process which is able to convert a wide variety of organic feed, such as coal, oil residues and biomass, into gaseous energy carrier [40]. As a zero net CO_2 energy source, biomass has become a promising feedstock for gasification [14, 41]. In recent decades, many studies focused on using gasification process to convert biomass into electricity and fuel gases, such as hydrogen and methane [42-44]. With the remarkable improvement in the design of gasifiers in recent years, few attempts have been made in commercial scale gasification-based biofuel production [45]. Therefore, it is necessary to update the economic feasibility analysis for converting biomass into transportation fuels by using the gasification pathway [46].

Gasification employs thermochemical processes to convert biomass into gaseous energy carrier, such as hydrogen, carbon monoxide, carbon dioxide and methane. A complex mixture of undesirable condensable hydrocarbons, also known as tar, also forms during the gasification process [47]. This mixture of gases is sent to a catalytic tar cracker to convert a portion of the undesirable tar into significantly more useful carbon monoxide and hydrogen [48]. These gases, also known as syngas, can be collected and upgraded to alcohols through mixed alcohol synthesis [49, 50]. These synthesized alcohols are then dehydrated and oligomerized into target hydrocarbon product, such as diesel and gasoline. Electric power can be generated during the gasification process by using CHP system to recover the process heat [44]. Figure 3 shows the overall process flow diagram for gasification scenario.

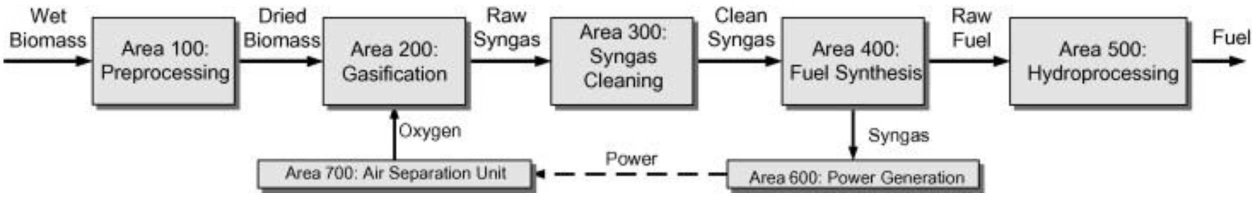

Figure 3 Overall process flow diagram for gasification scenario [51].

Gasification vs pyrolysis

Pyrolysis and gasification of biomass has been investigated for decades [52]. However, direct combustion of biomass such as wood is still being heavily used in many remote areas [53]. Since direct combustion is considered an inefficient and environmental detrimental pathway, the conversion of biomass into flammable gaseous and liquid fuel, such as gasification and pyrolysis, has received increasingly attention for commercial scale plants. Table 1 shows the comparison for pyrolysis and gasification pathway.

Table 1 Comparison of pyrolysis and gasification.

Pyrolysis	**Gasification**
Relatively cheaper	Require large capital investment [54]
Simple	complex
Relatively mature	Relatively new for biomass [52]
Low reaction temperature	High reaction temperature
Upgraded in liquid phase	Upgraded in gas phase
Absence of oxygen	Very little air or oxygen
Main products are char, bio-oil and flammable gases	Main products are synthesis gases, char and tars

Uncertainty and techno-economic analysis

Before each project is launched, the net present value needs to be calculated in order to understand the profitability associated with the project. This requires not only a full scale economical assessment, but also a technological feasibility evaluation. Techno-economic analysis (TEA) is an economical approach to understanding the cash flow regarding the consideration of technological risk [55]. Therefore the TEA has been widely used to assess and improve the viability for a system, such as the feasibility for building a commercial scale fast pyrolysis, gasification or hydrothermal liquefaction biorefinery [56-60]. In this study, TEA is employ to evaluate the net present value for *in situ* and *ex situ* catalytic pyrolysis scenarios as well as two gasification scenarios. The MFSP is then determined according to the results from the analysis.

Although TEA can provide an estimate on the MFSP, the results can vary within a wide range even for the same scenario [61-64]. Noticing that the MFSP is determined by multiple parameters, both the number of variables (parameters) and the level of detail for each parameter have positive influence on the MFSP. Therefore, the two following ways can increase the accuracy for the analysis on the MFSP: (1) instead of collecting single static values for key parameters, a distribution should be collected; (2) value for the same parameters should remain consistent across different scenarios. Although increasing the number of variables can also improve the accuracy of the analysis, the number of variables is predetermined by the parametric data available in literature and experiment, thus the influence of the number of variables on the result of the MFSP is not investigated in this study.

Reasons explained above show that the TEA along is not enough to provide sophisticated results for the MFSP. Furthermore, TEA only provides limited information over uncertainty, and a single net present value is not sufficient to reveal the potential economic risk related to the MFSP. Therefore, an uncertainty analysis is necessary to increase the accuracy of the results. Recent TEA studies have employed the Monte Carlo method for uncertainty analysis [63, 65, 66]. Monte Carlo analysis is a quantitative way to analyze the uncertainty level by generating random parameter samples according to their distribution. Although many studies investigated the techno-economic comparison for different biomass to transportation fuel pathways, few have employed stochastic simulations [51, 55, 61, 63, 64, 66-72].

Thesis Organization

This thesis consists of four chapters: Chapter one "General introduction", Chapter two "Techno-economic and uncertainty analysis of *in situ* and *ex situ* fast pyrolysis for biofuel production" (a journal paper published by Bioresource Technology), Chapter three "Understanding uncertainty of transportation fuel production via biomass gasification and mixed alcohol synthesis" (a journal paper published by Energy Technology), and Chapter four "General conclusion".

"Techno-economic and uncertainty analysis of *in situ* and *ex situ* fast pyrolysis for biofuel production" establishes an uncertainty and techno-economic analysis method for *in situ* and *ex situ* catalytic pyrolysis, yielding the estimated sensitivity and uncertainty range of the MFSP and net present value (NPV). It is also able to analyze the level of significance of key parameters, such as that internal rate of return, feedstock price, total project investment, electricity price, biochar yield and bio-oil yield. The primary researcher and author of this paper is Boyan Li; the corresponding author is Mark M. Wright.

"Understanding uncertainty of transportation fuel production via biomass gasification and mixed alcohol synthesis" modifies the method developed from the previous paper, and employs the technique to state-of-technology and target gasification scenarios. The primary author of this paper is Longwen Ou; the primary researcher and secondary author of this paper is Boyan Li; the corresponding author is Mark M. Wright.

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CAHPTER 2. TECHNO-ECONOMIC AND UNCERTIANTY ANALYSIS OF IN SITU AND EX SITU FAST PYROLYSIS FOR BIOFUEL PRODUCTION

Modified from a paper published in Bioresource Technology

Boyan Li[a], Longwen Ou[a], Qi Dang[a, b], Pimphan Meyer[c], Susanne Jones[c], Robert Brown[a, b], Mark Wright[a, b]

Abstract

This study evaluates the techno-economic uncertainty in cost estimates for two emerging technologies for biofuel production: *in situ* and *ex situ* catalytic pyrolysis. Stochastic simulations based on process and economic parameter distributions are applied to calculate biorefinery performance and biofuel production costs. The probability distributions for the minimum fuel-selling price (MFSP) indicate that *in situ* catalytic pyrolysis has an expected MFSP of $4.20 per gallon with a standard deviation of 1.15, while the *ex situ* catalytic pyrolysis has a similar MFSP with a smaller deviation ($4.27 per gallon and 0.79 respectively). These results suggest that a biorefinery based on *ex situ* catalytic pyrolysis could have a lower techno-economic uncertainty than *in situ* pyrolysis compensating for a slightly higher MFSP cost estimate. Analysis of how each parameter affects the net present value (NPV) indicates that internal rate of return, feedstock price, total project investment, electricity price, biochar yield and bio-oil yield are parameters which have substantial impact on the MFSP for both *in situ* and *ex situ* catalytic pyrolysis.

Introduction

Atmospheric CO_2 has increased more than 35% in the last century. It will pass the critical value of 550ppm in this century, unless fossil fuels consumption is significantly reduced [1, 2]. As one of the biggest greenhouse gas contributors, transportation fuels have received increasing attention in recent decades. Biomass-based transportation fuels have been considered as a clean and renewable alternative to fossil fuels. Under the authority of the Energy Independence and Security Act (EISA) of 2007, the revised Renewable Fuel Standard (RFS2) mandate requires the blending of biofuels for transportation applications. Commercial-scale biorefinery facilities are required to meet the goals set by EISA. Typically, large biorefinery projects processing 2000 metric tonnes per day of biomass or more, take more than four years to develop a design before startup [3]. Moreover, biofuel production facilities cannot be easily modified once they have been designed and constructed [4]. Therefore, a techno-economic analysis (TEA) across different platforms is needed in order to determine the most suitable pathway under given market conditions to avoid investing in enterprises with high commercialization risk. TEA can be used to understand and compare the profitability and breakdown cost for any project, therefore, it has been applied to many biorenewable systems such as corn ethanol production [5], gasification [6], pyrolysis [7], and hydrothermal liquefaction [8]. TEA of catalytic fast pyrolysis has received growing interest in recent years in particular. Previous studies show that the minimum fuel-selling price (MFSP) of biofuel produced by pyrolysis can vary within a fairly large range ($2 to $8 per gallon) [4, 9-11], which may be attributed to several reasons: (1) differences in system configurations, (2) variability in assumptions for parameter values, and (3) inconsistencies in approaches to address technical and market uncertainty [12].

Biomass fast pyrolysis and bio-oil upgrading technology is a promising way to convert cellulosic biomass into bio-diesel, bio-gasoline and other renewable fuels [13]. Two related catalytic pyrolysis configurations (*in situ* and *ex situ*) are receiving growing interest because of their ability to produce gasoline and diesel range hydrocarbons [14, 15]. The *in situ* catalytic pyrolysis system combines solid phase pyrolysis reactions and catalytic vapor upgrading within a single reactor. Whereas in *ex situ*, also known as vapor phase upgrading, fast pyrolysis occurs in a pyrolysis reactor and then the vapor phase goes into a separate catalytic reactor where vapors are catalytically upgraded [16].

The different configuration for *in situ* and *ex situ* catalytic pyrolysis leads to the following outcomes: (1) the total project investment for *ex situ* scenario is higher than the *in situ* case, due to the configuration complexity associated with the *ex situ* scenario; (2) the ex situ configuration separates the fast pyrolysis with catalytic vapor upgrading process, which minimizes the contact between biomass pyrolysis solid residue (char and ash) and catalyst, thus reducing the effects of coking and increasing the catalyst life span. As a result, the catalyst performance is improved and the maintenance expense for the catalytic reactor is reduced; (3) the liquid product as well as the organic liquid product obtained by the *in situ* and *ex situ* catalytic pyrolysis are similar, whereas the *in situ* catalysis pyrolysis has a noticeably better performance in producing phenols and aromatics, according to study by Yildiz and Ruddy [14, 17].

To our knowledge, the literature does not provide a TEA comparison of *in situ* and *ex situ* pyrolysis that accounts for the process performance variability of these technologies. In order to make a sensible comparison, the data for these systems should be normalized to a common basis. Moreover, sensitivity analysis alone is insufficient to address the uncertainty of the economic analysis since there are inherent uncertainties within each of the parameters. Therefore, model parameters should be represented by appropriate probability distributions instead of static values to improve the representation of potential analysis outcomes. One of the most straightforward ways to apply uncertainty analysis is by using Monte Carlo simulation [18, 19]. Monte Carlo simulations generate parameter samples randomly to quantitatively analyze the output uncertainty level. Although there are numerous comparison studies that evaluate biomass to transportation fuel pathways, few have incorporated the use of stochastic simulations [4, 6, 7, 10-12, 20, 21].

The objective of this paper is to create a side-by-side techno-economic comparison of *in situ* and *ex situ* catalytic pyrolysis scenarios that addresses both sensitivity and uncertainty analysis in the comparison of these technologies. In this study, we (1) collect technical and historical data for key process and economic parameters, (2) conduct stochastic runs of chemical process models for *in situ* and *ex situ* catalytic pyrolysis, (3) investigate the sensitivity range and uncertainty of the MFSP and NPV, and (4) analyze the level of significance of these parameters to the MFSP.

Methods

Overall process description

This study utilizes the method developed by Brown and Wright [12] and expands it to include process parameters and analyze parameter significance level. In general, this study involves four steps: (1) collecting probability distributions for key parameters; (2) modifying existing chemical process and economic models to enable stochastic evaluations; (3) developing best-fit distributions of the stochastic MFSP and NPV, and (4) analyzing the significance level of model parameters. Figure 4 illustrates the various steps involved in this analysis. First, historical and experimental data for key parameters are collected and adjusted. Second, best-fit distributions of key parameters were calculated and data sets with 10,000 random values for each key parameter according to their best-fit distributions were generated using Mathematica^{TM}. Third, a Visual Basic for Applications (VBA) interface was developed to import all the generated data sets of parameter values into CHEMCAD^{TM}, instruct CHEMCAD^{TM} to run through samples from the data sets, and record the corresponding output of key mass and energy results from CHEMCAD^{TM}. The MFSP of biofuels were calculated by integrating outputs from CHEMCAD^{TM} into a 30 year discounted cash flow rate of return financial spreadsheet. Finally error bars and distributions of the MFSP, and the relative impacts of the key input parameters were determined by analyzing these economical spreadsheets and conducting the uncertainty analysis.

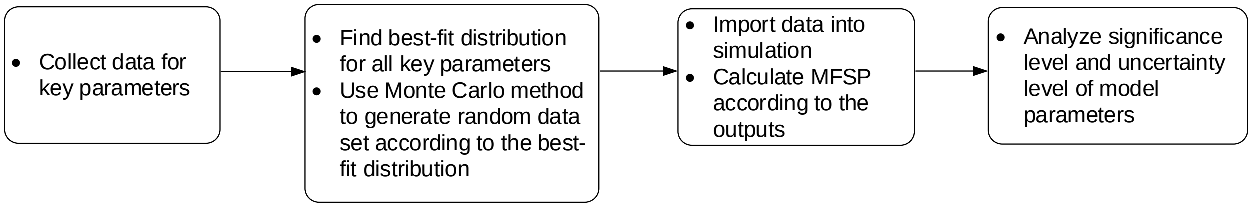


Figure 4 Flowchart description of the uncertainty analysis methodology for catalytic pyrolysis scenarios.

Data collection

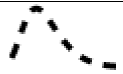
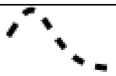
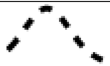
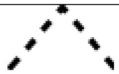
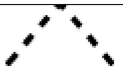
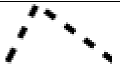
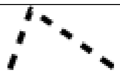
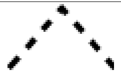
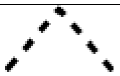
There are hundreds of parameters involved in TEA of biofuel pathways. The scope of this study is limited to parameters with known significant impact on process profitability as identified by the Pacific Northwest National Laboratory (PNNL) [22], and parameters with publically available data. The list of selected parameters is shown in Table 2.

There were some parameters applied to both *in situ* and *ex situ* cases. Historical wholesale price for feedstock and various fuels from 2007 to 2012 were gathered based on the following sources. The Energy Information Administration (EIA) provides U.S. average wholesale prices for gasoline and diesel, and industrial natural gas and electricity prices [23, 24]. Feedstock price data are based on pine pulpwood prices from the Texas Forestry Service, and the mean value of the feedstock price was shifted to $80/MT [25]. The remaining data (catalyst to biomass ratio, hydrotreating yield, first stage Hydrodeoxygenation (HDO) catalyst cost, second stage HDO catalyst cost, second Stage HDO Liquid Hourly Space Velocity (LHSV), total project investment factor, hydrotreating catalyst life, compression requirement factor, and hydrogen consumption factor) were gathered from a Pacific Northwest National Laboratory (PNNL) report [22].

Energy commodity prices exhibit significant volatility due to the complex nature of the energy market [26]. This volatility can be captured by appropriate probability distributions. Several candidate distributions were considered: Normal, Lognormal, Exponential, Chi-Square, Cauchy, Laplace, and Logistic. The best fit distributions were determined from the Anderson-Darling test [27]. A similar approach was employed to determine the best-fit distributions for other selected key processing parameters. In some cases, the best-fit distributions were adjusted to account for differences in the expected mean value, variance, or distribution type.

Table 2 lists the best-fit distributions, mean, 10% and 90% confidence values for process and economic parameters. This approach relies on the assumption that historical volatility is an indicator of future volatility, and variability gathered from literature data is representative of the uncertainty in a commercial system. Limitations from these assumptions are impossible or expensive to address because of the nature of commodity markets and the difficulty of gathering experimental data for all possible process configurations.

Table 2 Probability density functions (PDF), mean, and ±10% confidence level values of key parameters that apply to both *in situ* and *ex situ* cases.

Parameter	Distribution		Mean	Confidence (10%)	Confidence (90%)
Industrial Natural Gas Price ($/mcf)		Lognormal	6.24	3.93	8.95
Industrial Electricity Price (¢/kwh)		Normal	6.05	5	7.09
Pine pulpwood ($/MT)		Lognormal	78.69	67.21	90.18
Gasoline Wholesale ($/gallon)		Lognormal	1.78	0.89	2.89
Diesel Wholesale ($/gallon)		Lognormal	1.76	0.59	2.92
Catalyst to Biomass Ratio		Triangular	3.83	1.23	7.08
Hydrotreating Yield (wt. %)		Triangular	0.44	0.43	0.45
First Stage HDO Catalyst Cost ($)		Triangular	60	43.42	76.58
Second Stage HDO Catalyst Cost ($)		Triangular	18.5	13.32	24.61
Second Stage HDO LHSV (1/h)		Triangular	0.24	0.16	0.33
Capital Cost ($)		Triangular	1.1	0.97	1.26
Hydrotreating Catalyst Life (years)		Triangular	1.17	0.77	1.61
Compression Requirement Factor		Triangular	1	0.89	1.11
Hydrogen Consumption Factor		Triangular	1	0.89	1.11

Literature data from a number of sources were employed to estimate the distribution for gas, liquid and solid products from the *in situ* catalytic fast pyrolysis of biomass [17, 28-39]. Figure 5 shows the *in situ* catalytic pyrolysis organic oil yield and oxygen content reported in the public literature. The variability in the data reflects a diversity of experimental methods and reactor designs. Best-fit distributions of organic oil (bio-oil) yield and biochar were determined based on the data reported in literature. The non-condensable gas yield was adjusted to maintain a closed mass balance across the pyrolysis process.

Mante *et al* [34] conducted pyrolysis experiments using crystalline Y-zeolite based catalysts with a fluidized bed reactor and hybrid poplar wood as feedstock. The organic oil yields from his studies ranged between 13.8% and 41.5%. The experiments lead by Agblevor [29] had an organic oil yield of 21%. A fluidized bed pyrolysis reactor and HZSM-5 acidic catalysts were used in this study, while hybird poplar wood samples served as feedstock. Paasikallio's group [37] employed a fluidized bed pyrolysis reactor with ZSM-5 acidic catalysts and forest thinnings. In their experiments, the organic oil yield varied between 14% and 49%. Mullen *et al.* [36] conducted catalytic fast pyrolysis experiments using a fluidized bed reactor with white oak wood as feedstock. Two catalysts were chosen in this study: Ca^{2+} exchanged Y zeolite and a proprietaryβ-zeolite type catalyst (catalyst M), which lead to 17% and 11% organic oil yields respectively. A conical spouted-bed reactor with a HZSM-5 catalyst was employed by Olazar's group [39]. The organic oil yield from this study is 30.8% with pine sawdust as the feedstock.

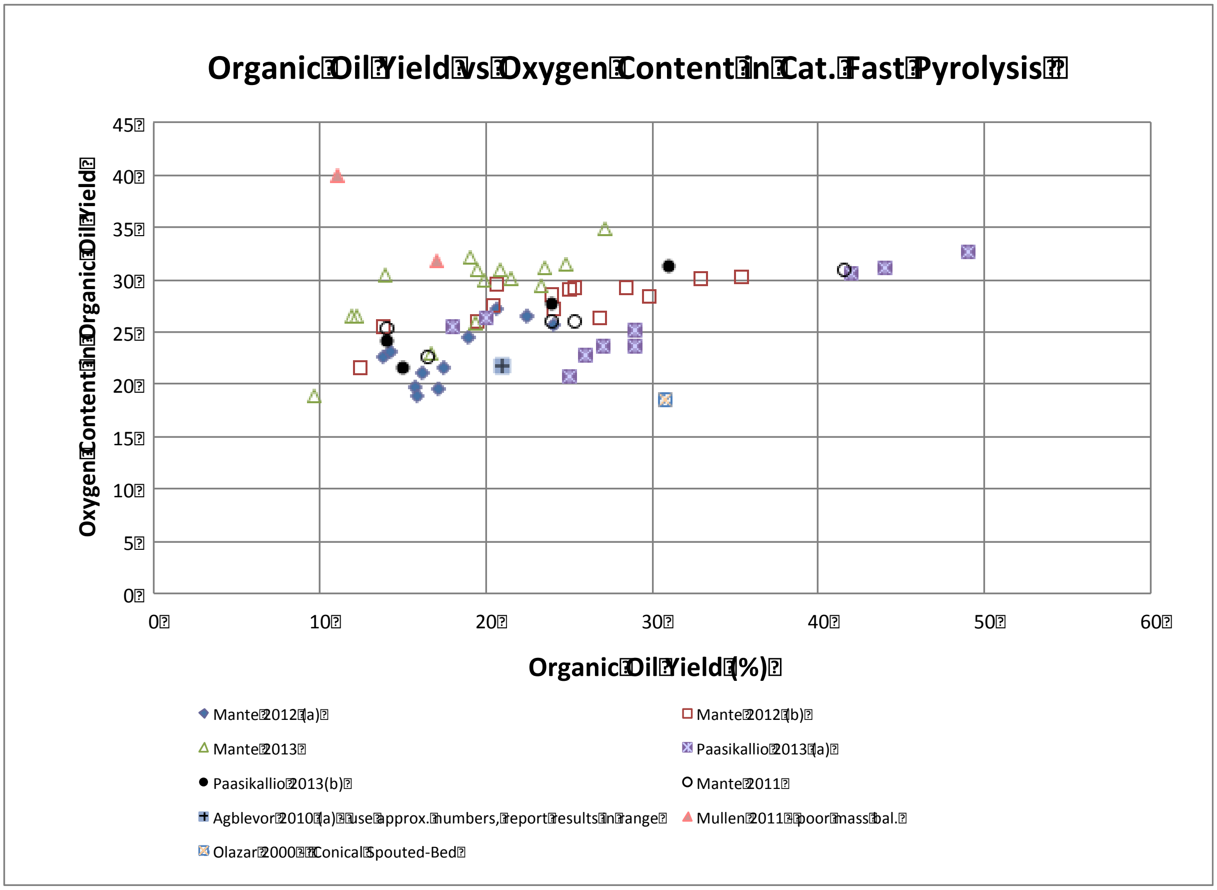


Figure 5 *In situ* catalytic pyrolysis organic oil yield and oxygen content reported by various sources.

There is limited *ex situ* data available in the literature compared to *in situ*. Researchers at the National Renewable Energy Laboratory (NREL) have obtained comparable pyrolysis oil yields from *ex situ* catalytic pyrolysis as *in situ* under similar operating conditions. Therefore, this study adjusts the *in situ* to reflect the similarity in yields from recent *ex situ* catalytic pyrolysis experiments at NREL. To obtain the *ex situ* distributions, the *in situ* distribution mean was shifted to the expected *ex situ* yield and the variance was lowered based on engineering judgment. *Ex situ* experiments have shown more consistent yield results than *in situ* by avoiding contact between catalysts and biomass, char, and ash. Figure 6 shows the comparison of biochar and bio-oil yield (wt. %) distributions between *in situ* and *ex situ* cases. Pyrolysis non-condensable gas yields are determined by difference. The mean bio-oil yields for both *in situ* and *ex situ* cases are around 43 wt.%.

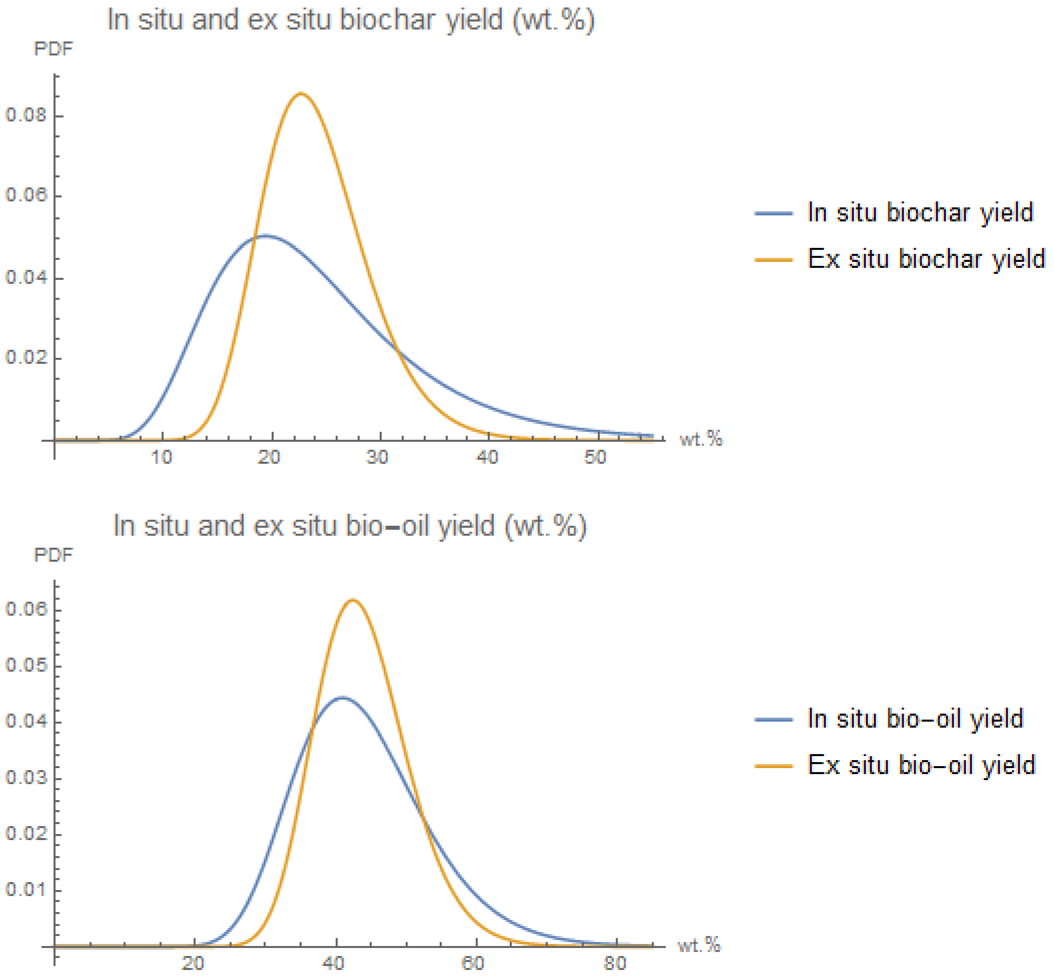


Figure 6 Comparison of biochar and bio-oil yield (wt. %) between *in situ* and *ex situ* cases.

Modeling and analysis

In situ and *ex situ* CHEMCAD^{TM} models for 2000 dry metric ton biomass per day biorefineries were developed by PNNL and Iowa State University (ISU). The catalytic pyrolysis process for producing gasoline and diesel is described in Figure 7. The *in situ* configuration conducts the fast pyrolysis and catalytic vapor upgrading processes within the same reactor. The *ex situ* configuration employs a separate catalytic vapor phase upgrading reactor system, as shown in figure 7, right after the non-catalytic fast pyrolysis reactor.

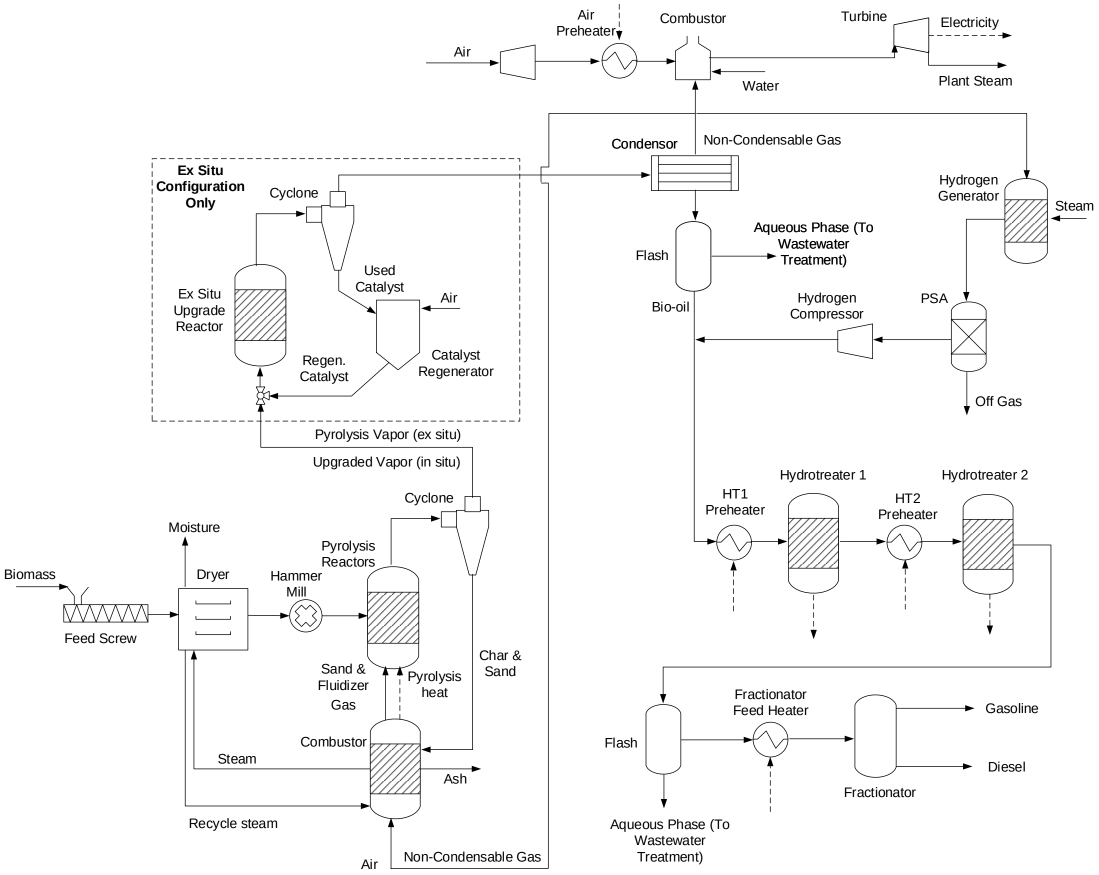


Figure 7 Process diagram for production of transportation biofuel via *in situ* and *ex situ* catalytic pyrolysis.

Data sets consisting of 10,000 samples of bio-oil and biochar yields for both *in situ* and *ex situ* were obtained based on the distributions shown in Figure 6. The generated bio-oil and biochar yield data sets for *in situ* and *ex situ* were applied to the *in situ* and *ex situ* CHEMCAD^{TM} models respectively. Excel VBA code was developed to import the stochastic samples of parameter values into CHEMCAD^{TM}, and record the corresponding output of key mass and energy results from CHEMCAD^{TM}. These outputs were integrated into financial spreadsheets to calculate production costs and the biofuel MFSPs. Mathematica^{TM} was employed to analyze the financial spreadsheets and conduct the uncertainty analysis. Uncertainty analysis results were reported as error bars and distributions of the MFSP, and the relative impacts of the key input parameters. P-values were employed to determine the significance of model parameters using a 0.05 threshold.

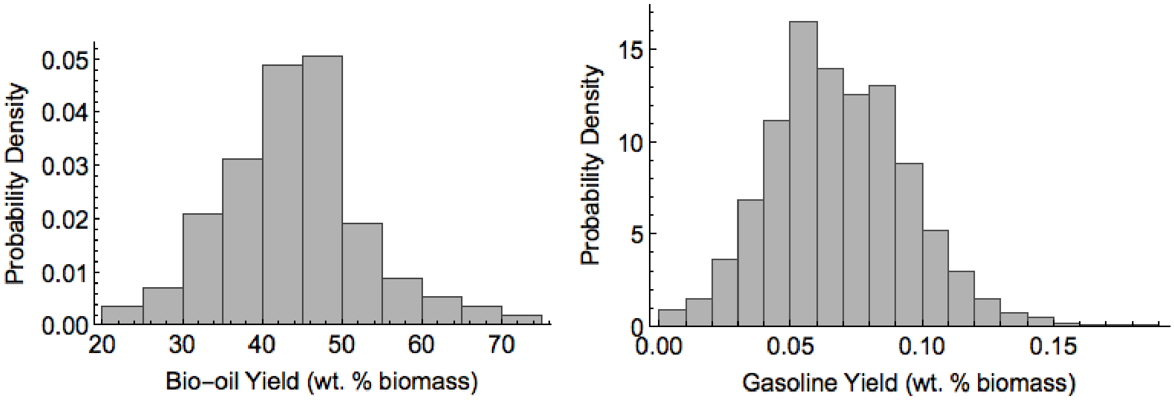
Results and Discussion

The *in situ* and *ex situ* catalytic pyrolysis models for 2000 MTPD of biomass input estimated average pyrolysis oil yields of 438 and 438.7 kg/BDMT respectively. These similar yields are based on adjusting the *ex situ* yields to match *in situ* pyrolysis as discussed in personal communication with researchers at NREL. Pyrolysis biofuel yields of 40.3 and 37.9 gallons per dry MT of feedstock were obtained. Table 3 describes the key process material yields for the *in situ* and *ex situ* catalytic pyrolysis processes.

Table 3 Key process material yields for the in situ and ex situ catalytic pyrolysis process.

Scenario	In Situ	Ex Situ
Gas Species (kg/BDMT)	321.2	320.3
Pyrolysis Oil (kg/BDMT)	438.0	438.7
Char (kg/BDMT)	240.8	241.0
Natural Gas Utilized (MT/day)	73.85	NA
Gasoline & Diesel Blendstock Yield (wt. % dry biomass)	12.6	13.5
Gasoline & Diesel Blendstock Yield (gal/dry MT)	40.3	37.9

The *in situ* bio-oil yield probability distribution is shown in Figure 8 (a), while the simulated yield of gasoline from the *in situ* process model is presented in Figure 8 (b). These results indicate that there is a strong relationship between the bio-oil and gasoline yields, but intermediate upgrading steps affect the shape of the final distribution. At low bio-oil yields, the majority of recovered hydrocarbons are in the diesel and fuel oil range and the gasoline yield decreases.



(a)

(b)

Figure 8 *In situ* catalytic pyrolysis bio-oil yield (a) and simulated gasoline yield (b).

Figure 9 shows the mass flow rates for *in situ* and *ex situ* cases. The mass flow rates for the *ex situ* case are shown in parentheses while the mass flow rates for the *in situ* case are shown without parentheses. Overall, the rate of mass conversion to fuels for the in situ and ex situ are 12.6 wt. % and 13.5 wt. % respectively, which indicates that the *ex situ* process could have a higher production rate than *in situ* pyrolysis.

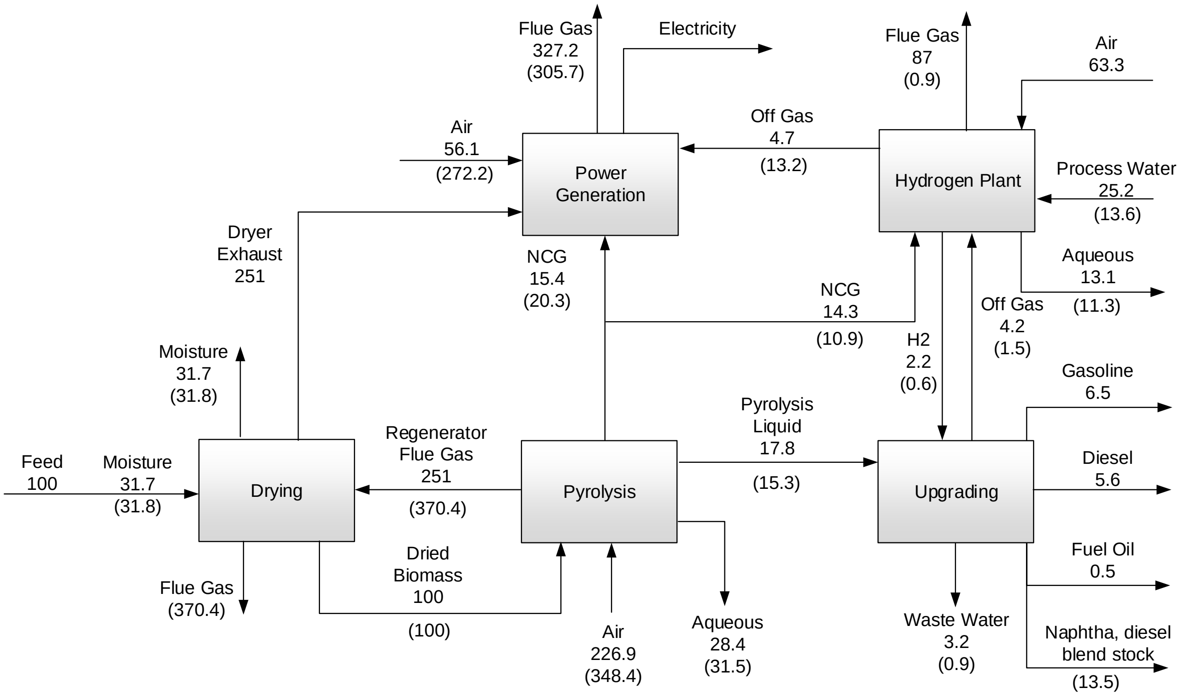


Figure 9 Material flow rates for *in situ* and *ex situ* (shown in parenthesis) catalytic pyrolysis process.

The MFSP probability and cumulative distributions for the *in situ* and *ex situ* cases are shown in Figure 10. The dark shaded regions indicate 10% to 90% confidence intervals, and the dashed vertical line shows the base case values, which indicates the baseline value for the MFSP determined from previous efforts at ISU. The base case MFSP for the *in situ* scenario is $3.69/gal, whereas, from the uncertainty analysis of this study, a mean value of $4.2/gal is calculated with a standard deviation greater than 1. In the *ex situ* case, a mean value of $4.27/gal was calculated from the uncertainty analysis. The base case value of $5.31 falls outside the 90% confidence interval of the uncertainty MFSP distribution as figure 10 (b) indicates. The high MFSP base case value found in *ex situ* scenario is based on literature data for bio-oil yield; recent developments at the national laboratories indicates higher *ex situ* pyrolysis yields leading to lower MFSP estimates [16]. Furthermore, differences in the mean and baseline MFSP values are due to the use of probability parameter distributions instead of standard techno-economic assumptions.

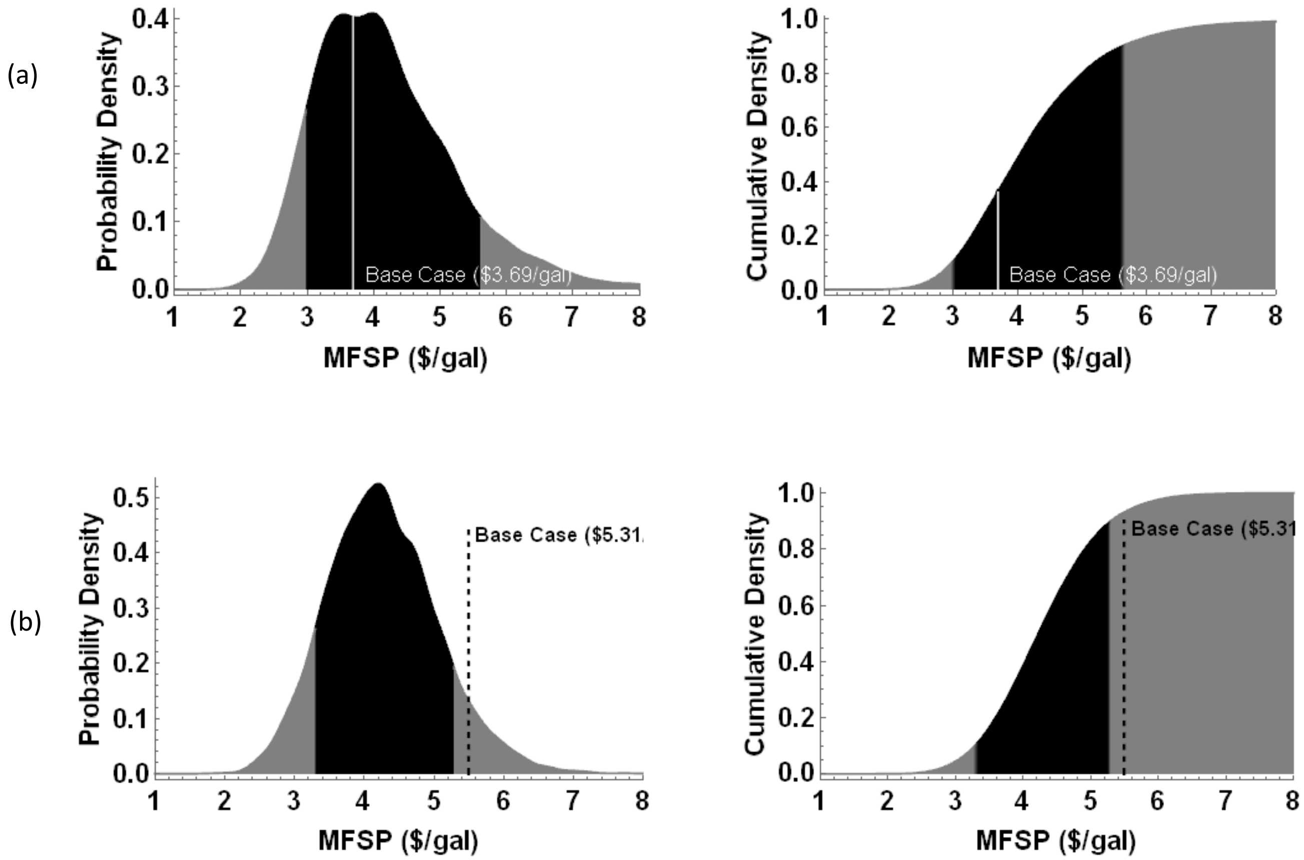


Figure 10 *In situ* (a) and *ex situ* (b) catalytic pyrolysis Minimum Fuel-Selling Price (MFSP) probability and cumulative density functions. Confidence levels of 10 and 90% are indicated by the dark shaded region.

The uncertainty tornado chart in Figure 11 shows the *in situ* catalytic pyrolysis parameter uncertainty impact on MFSP. Bold legends indicate parameters with high significance at the 0.05 p-value level. The tornado chart features box plots with gates that indicate the minimum and maximum ranges of the MFSP based on changes to each parameter value. The min/max ranges are analogous to the values derived from a sensitivity analysis. The colored box areas are the

0.25 and 0.75 quartile region of MFSP values for the given parameter. The vertical white lines indicate the mean MFSP value. Figure 11 highlights important differences with traditional sensitivity analysis plots (traditional tornado charts). Traditional sensitivity analysis can only indicate the minimum and maximum ranges of MFSP changes by varying each parameter. However, the historical data and experimental data collected in this study suggest that the minimum and maximum value for each parameter are less likely to occur than the values within the 0.25/0.75 quartile, which indicates that parameters with a wide range of values may have much narrower influence on MFSP than expected. For example, feedstock cost has a wider range of possible MFSP values than Internal Rate of Return (IRR) and total project investment, but a narrower range within the 0.25/0.75 quartiles than IRR and total project investment. This suggests that feedstock cost may have a lesser influence on the MFSP than other financial assumptions. Furthermore, this new approach is able to determine whether a parameter tends to have a positive or negative influence on the MFSP. For instance, the feedstock distribution is skewed towards lower MFSP values and is therefore more likely to result in a lower MFSP than the average feedstock cost would suggest. This finding contrasts with traditional sensitivity analysis, which does not provide any likelihood information for the range of MFSP values.

The uncertainty tornado chart ranks parameters by their influence on MFSP with the largest direct influence (higher parameter values leading to higher MFSP) shown at the top and largest inverse influence shown at the bottom. For examples, higher electricity prices reduce the MFSP because *in situ* catalytic pyrolysis exports electricity to the grid; higher hydrotreating catalyst life also reduces the MFSP due to the reduction of hydrotreating catalyst replacement costs per year; higher biochar yield has an inverse impact on MFSP because it correlates with a lower bio-oil yield, which leads to a lower upgraded fuel production. Among all the parameters, bio-oil yield has a significantly wider range of both possible MFSP values and 0.25/0.75 quartile values than other parameters, which suggests that bio-oil yield has a dominant impact on the MFSP. It is notable that some of the minimum possible MFSP values caused by bio-oil yield changes are below zero. This suggests that in some cases, although statistically unlikely, the biorefinery facility could make sufficient profits from the sale of a co-product such as electricity.

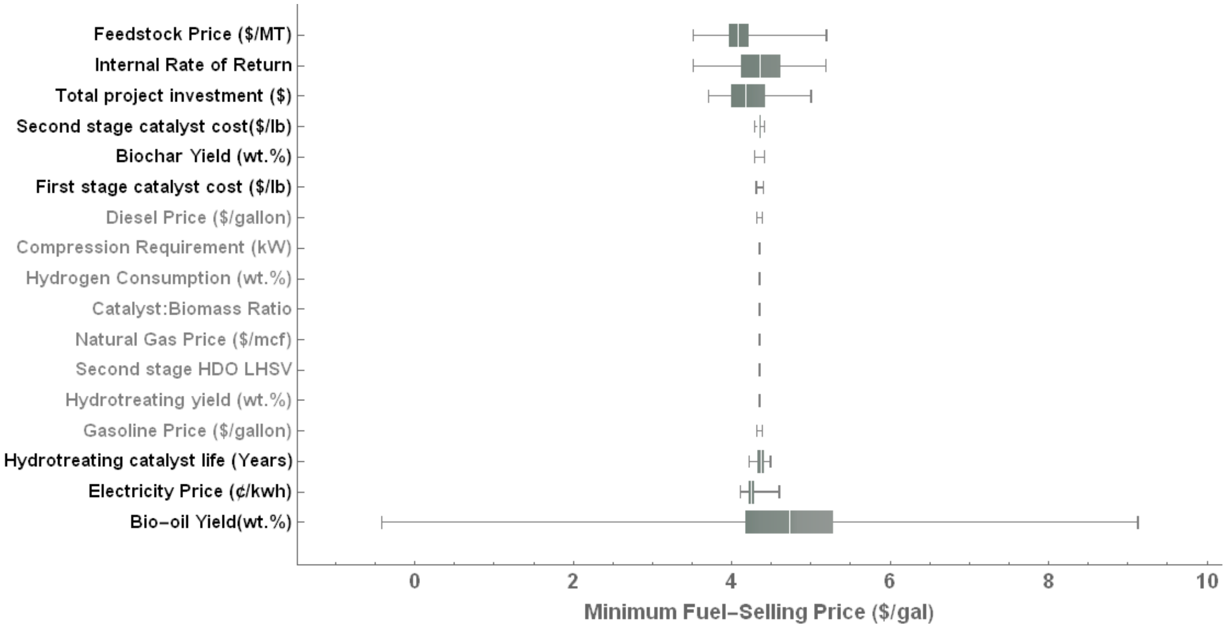


Figure 11 *In situ* catalytic pyrolysis parameter uncertainty impact on the MFSP. Gates indicate min/max MFSP range; boxes indicate 0.25-0.75 quantiles of the MFSP; white vertical lines show the mean MFSP value. Bold legends indicate significant ($p<0.05$) parameters.

The uncertainty tornado chart for the *ex situ* pyrolysis scenario is shown in Figure 12. In this case, IRR and total project investment have wider 0.25/0.75 quartile MFSP value ranges than feedstock price. Therefore, IRR and total project investment may have greater impact on the MFSP. Electricity is generated in the *ex situ* case, therefore, electricity consumption, which is a negative value, has positive impact on MFSP and electricity price has an inverse impact on

MFSP. Higher biochar yield has an inverse impact on MFSP due to the same reason discussed in *in situ* case.

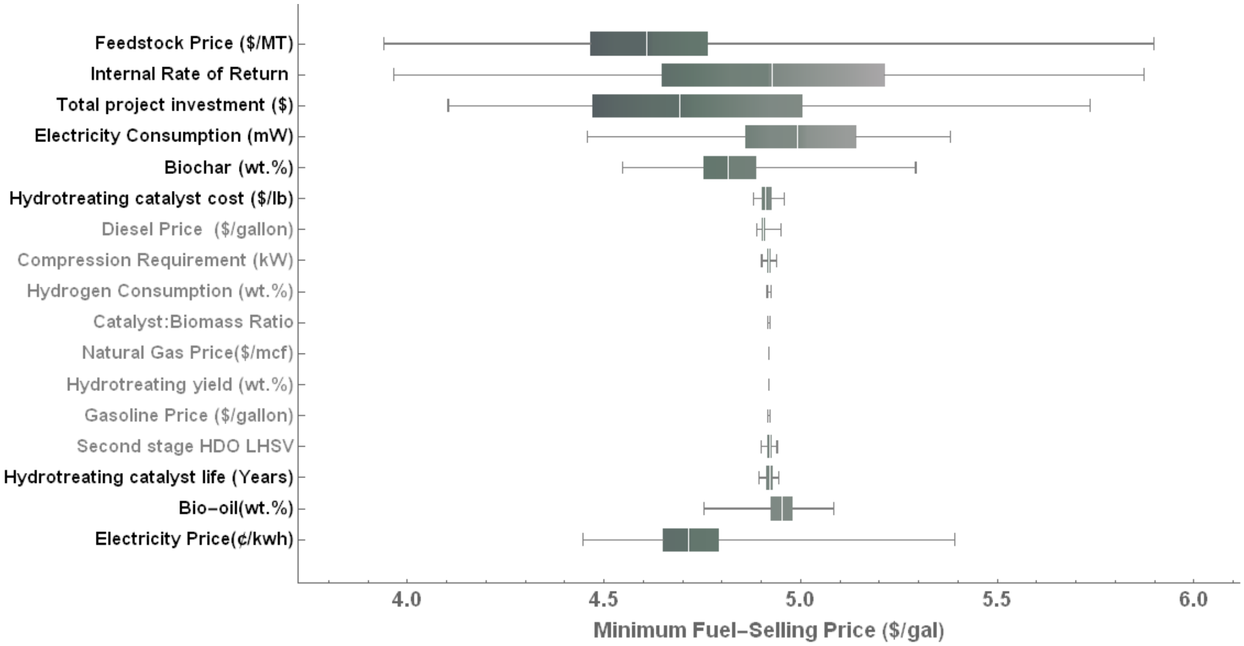


Figure 12 Ex situ catalytic pyrolysis parameter uncertainty impact on the MFSP. Gates indicate min/max MFSP range; boxes indicate 0.25-0.75 quantiles of the MFSP; white vertical lines show the mean MFSP value. Bold legends indicate significant ($p<0.05$) parameters.

Figure 13 demonstrates the side-by-side MFSP comparison for the *in situ* and *ex situ* scenarios based on previous studies (a) and this study (b). The dots indicate the mean of the MFSP, while the lines indicate standard deviation. In the initial analysis, data from previous research in our groups and literature available in 2012 were selected and the same uncertainty analysis methods described in this paper were employed. As figure 13 (a) shows, this initial analysis suggests that *in situ* catalytic pyrolysis might be more economic than *ex situ*, with the expected MFSP of $4.2 per gallon and $5.31 per gallon respectively. Both cases have large error bars (greater than $1 per gallon), which indicate large uncertainty. Figure 13 (b) is a revision of the analysis that was informed by recent experimental data as discussed in the method section. These results indicate that *in situ* and ex situ catalytic pyrolysis are expected to have a similar MFSP, \$4.2 per gallon and \$4.27 per gallon respectively. This uncertainty analysis suggests that *ex situ* catalytic pyrolysis is expected to have a smaller standard deviation than *in situ* catalytic pyrolysis, therefore, there could be greater techno-economic risk associated with the *in situ* case.

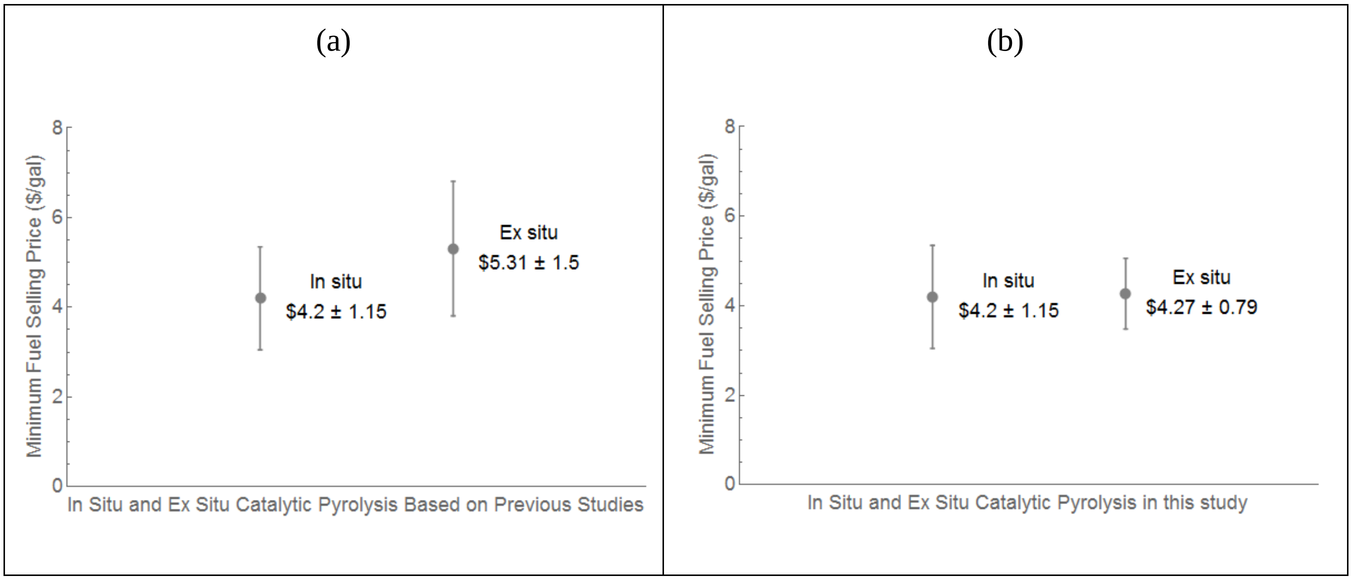


Figure 13 The error bar of MFSP for *in situ* and *ex situ* catalytic pyrolysis based on previous studies (a) and the most recent results (b).

Conclusion

This techno-economic study calculates and compares two different catalytic fast pyrolysis pathways: *in situ* and *ex situ*. Best-fit distributions and Monte Carlo methods are employed in to investigate the impact of parameter uncertainties on biofuel MFSP estimates. VBA and CHEMCAD^{TM} interfaces are employed to simulate the biomass catalytic pyrolysis and upgrading process. Probability distributions for the MFSP and significance levels for simulations parameters are determined and investigated.

Uncertainty analysis shows that *in situ* catalytic pyrolysis is expected to have a similar MFSP with *ex situ* catalytic pyrolysis, $4.2 per gallon and $4.27 per gallon respectively. However, *in situ* catalytic pyrolysis has a greater standard deviation for MFSP compared to the *ex situ* catalytic pyrolysis scenario, which indicates potential for greater techno-economic risk.

Sensitivity and uncertainty analyses indicate that internal rate of return, feedstock price, total project investment, electricity price, biochar yield and bio-oil yield have significant impact on the minimum fuel-selling prices for both *in situ* and *ex situ* catalytic pyrolysis.

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CHAPTER 3. UNDERSTANDING UNCERTAINTY OF TRANSPORTATION FUEL PRODUCTION VIA BIOMASS GASIFICATION AND MIXED ALCOHOL SYNTHESIS

Modified from a paper submitted to Energy Technology

Longwen Ou[1], Boyan Li[1], Qi Dang[1,2], Susanne Jones[3], Robert Brown[1,2], Mark M. Wright[1,2*]

Abstract

This analysis evaluates uncertainties of previously conducted techno-economic analysis of transportation fuel production via biomass gasification and mixed alcohol synthesis. Two scenarios are considered: a state-of-technology scenario utilizing existing technologies and a target scenario representing future advancements in related technologies. Uncertainties of more than ten parameters are investigated, including feedstock price, internal rate of return (IRR), etc. Historical price data of these parameters are fitted with the most appropriate distribution and datasets are generated for each parameter accordingly. These data sets are then utilized to run a Monte-Carlo simulation. The results yield minimum fuel selling prices of $7.02/gal with a standard deviation of 0.49 for the state-of-technology scenario and $4.33/gal with a standard deviation of 0.42 for the target scenario respectively. Feedstock price and IRR have significant impact on the minimum fuel selling price in both scenarios. Although only investigated in the target scenario, Lang Factor is the second most impactful parameter, following feedstock price.

Introduction

Increasing emphasis on the environment and growing demand for substitute of fossil fuels have make biofuels more attractive than ever in the history [1-3]. Except for bioethanol that has been produced commercially, a wide variety of pathways have been investigated, including gasification, fast pyrolysis, and hydrothermal liquefaction [4-8]. Gasification of biomass is a desirable technology for its ability to deliver a wide range of fuels through different upgrading pathway, such as Fischer-Tropsch, mixed alcohol synthesis and fermentation [9-13]. Among them, biomass gasification and mixed alcohol synthesis is an attractive pathway for biofuel production due to its ability to produce ethanol at a high yield [9]. Although gasification is a mature technology, catalytic upgrading for biofuels production is still in varying levels of development. Moreover, high initial capital investment and challenges with tar removal are common barriers to commercial success for biomass gasification plant. Therefore it is imperative that profitability and technic feasibility of gasification pathways are investigated before investments are made to minimize risks.

Techno-economic analysis (TEA) has been used widely to evaluate economic feasibility of various biofuel pathways, including mature traditional first generation ethanol production, and relatively new fast pyrolysis, gasification, and hydrothermal liquefaction [14-18]. TEA is recognized as a useful tool to help understand the economics lying beneath proposed processes and avoid potential risk of investment. It assists in identifying the most profitable pathway and potential ways to improve the profitability of a particular pathway by better understanding the composition of capital and operating costs.

TEA is usually utilized to evaluate profitability of early stage processes. Immaturity of these processes dictate their intrinsic uncertainties, which result from uncertainties of the parameters chosen to conduct the TEA such as feedstock price, internal rate of return (IRR), etc. An informative TEA should thus be capable of not only measuring the profitability of the process being evaluated but also quantifying the uncertainty of itself. However, most TEAs previously conducted fail in this respect. To start with, price volatility was neglected in most TEAs since it is assumed that prices of feedstock, chemicals and fuels are constant while the fact is commodity prices can vary significantly even in a small time span. Furthermore, most TEAs utilizes predetermined financial assumptions in which all the parameters are also constant. Therefore, most TEAs presented the result as a number with complete certainty [19].

Most TEAs include sensitivity analysis, in which a single predetermined parameter is manipulated to take a small number of values (usually 3 values) while all other parameters remain the same to investigate how much impact each parameter can have on the final result. Despite the fact that sensitivity analysis helps understand the impact of each parameter on the final result, in practice multiple parameters vary simultaneously. Besides, each parameter only takes a small number of different values in sensitivity analysis, which is insufficient to reflect interactions between parameters. Furthermore, a sensitivity analysis does not provide any information on the probability distribution of the parameter investigated. Consequently, an alternative approach is required to comprehend the relationships between model parameters and the TEA performance.

Monte-Carlo simulation has been adopted in recent TEAs as an effort to account for the uncertainties within the analyses [15, 20, 21]. It proceeds as follows: several key parameters with potential for significant impact on the results are first identified; a predetermined distribution is then assigned for each parameter; large data sets (usually 10,000 data) are generated according to the assigned distributions. These data sets are then incorporated into the financial spreadsheet to run a Monte-Carlo simulation so that each iteration utilizes a unique combination of data of each parameter in the data set [22]. It allows more than one parameter to vary at the same time so that impacts of multiple parameters on the result can be evaluated. It also provides distribution information on the result of TEA. Nevertheless, most of the previous TEAs utilized predetermined probability distributions for the parameters, which does not necessarily represent the true distributions of the parameters considered [19].

This paper tackles the problems identified in previous TEAs by developing a detailed uncertainty analysis of two gasification scenarios: a state-of-technology scenario and a target scenario. More than ten parameters that may have significant impact on the MFSP are investigated. Distributions of each parameter are determined from historical data, which are then used to generate data sets for Monte-Carlo simulations.

Methodology

Process design

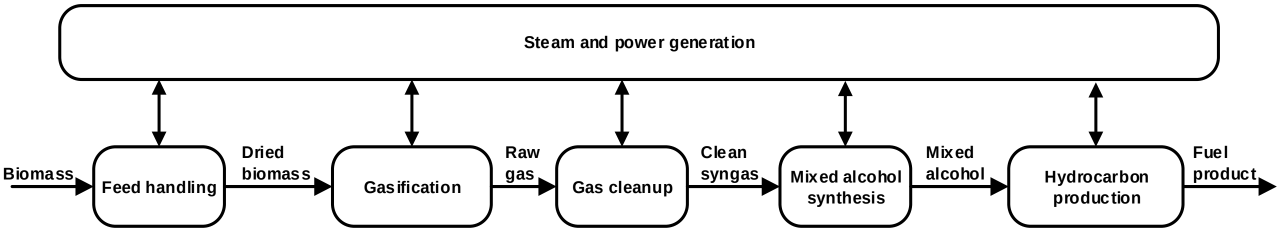

Figure 14 Schematic of biomass gasification and alcohol synthesis for diesel fuel production.

The process evaluated in this analysis is transportation fuel production via biomass gasification and subsequent alcohol synthesis and conversion to distillates. Six areas are involved in this process: feed handling and preparation, gasification, syngas cleanup, mixed alcohol synthesis, hydrocarbon production, and steam and power generation, as shown in Figure 14. The design of feedstock handling, gasification, syngas cleanup, and mixed alcohol synthesis is based on previous work by NREL [9]. The design of hydrocarbon production is based on related patents.

Feed handling and preparation involves feedstock drying to below 10 wt. % moisture content. The dried biomass is then gasified at 870 ℃ and 2 bar. A relatively small fraction of biomass is converted into tars, which are comprised mostly of aromatic and poly-aromatic hydrocarbons. The nitrogen in the feedstock is primarily converted to ammonia. The raw producer gas from the gasifier is sent to a catalytic tar reformer to convert a portion of tar, methane and other light hydrocarbons to CO and H2. Part of the ammonia is converted to nitrogen and hydrogen. The syngas is then cooled and sent to a wet scrubber to remove impurities such as particulates, remaining ammonia and residual tars.

The conditioned syngas is then compressed to 207 bar using a six-stage compressor system with inter-stage cooling. The compressed syngas is mixed with recycled syngas and recycled methanol and preheated to 313 ℃ before entering for mixed alcohols reactor. The gas entering the alcohol synthesis reactor has a H2/CO molar ratio of 1.5. Steam is generated using the heat released from the exothermic alcohol synthesis reactions. The effluent gases from the reactor are cooled and flashed to remove alcohols as a liquid stream. The gaseous stream is recycled to the reactor after removal of CO2 and H2S with a physical solvent: dimethyl ethers of polyethylene glycol (DEPG). The solvent from the absorber is then flashed at a lower pressure to expel less soluble compounds such as H2, CO, and CH4, which is then recycled to the tar reformer and fuel combustor. The liquid effluent is directed to a distillation column for methanol removal before dehydration. Overhead product of the methanol removal column, consisting of essentially all of the feed methanol and other light compounds such as CO2 and H2, is then cooled and flashed. The gaseous stream of the flash drum goes to fuel combustor with the liquid stream, which consists mostly of methanol and a small amount of ethanol, recycled to the mixed alcohol synthesis reactors.

Dehydration of mixed alcohols is designed based on US patent 4396789 and US patent application 20130190547. The synthesized alcohols are pumped to 20 bar and dehydrated in a series of three adiabatic reactors to produce small molecular weight olefins. After heat recovery, the olefin product from the dehydration reactors goes through a water scrubber for removal of methanol and other residual alcohols. The olefin stream undergoes oligomerization in the presence of organic solvent, toluene, at 32 bar to produce linear alpha olefins including 1-decene and 1-dodecene.This process is based on patent DE4338414C1.

The product stream is depressurized and cooled in a flash separator. The gaseous stream is recycled to the oligomerization reactor while the liquid stream is directed to a distillation column to separate solvent from olefins. The solvent is recycled to the oligomerization reactor. The olefins are hydrogenated at 29 bar to produce saturated hydrocarbons product.

The process also includes a steam cycle that generates steam through recovering waste heat from the hot process streams throughout the plant. The steam cycle also generates power for plant operations through a multi-stage steam turbine. A fuel combustor is also included to recover energy from plant off-gases.

State-of-technology scenario vs. target scenario

This analysis involved two scenarios: a state-of-technology scenario and a target scenario. The state-of-technology scenario was designed based upon existing technology. A high Lang Factor (total investment divided by bare equipment costs) of 4.15 was used in this case to account for the high degree of uncertainty in the process equipment needed and costs at such an early stage of analysis. In the target scenario, lower equipment costs were assumed to account for technological advancements. The uncertainties in the Lang Factor were also evaluated in the target scenario to see its impacts on the MFSP. A lower mean value of 4 was assumed for Lang factor than the fixed value in the state-of-technology scenario. Another difference between the two scenarios is the oligomerization conversion as discussed in a later section.

Uncertainty analysis

This analysis evaluates uncertainties of previously conducted TEAs of gasification and subsequent production of transportation fuels. Uncertainties of the TEAs result from various factors including uncertainties in parameters such as IRR, capital costs and volatility of feedstock and product prices. Uncertainties of more than ten parameters are considered in this analysis to gain a better understanding of the economic performance of the proposed process, including feedstock price, IRR, capital cost, Lang Factor, catalyst cost, electricity price, conversions of key reactions such as mixed alcohol synthesis reactions and olefin oligomerization reactions, etc. The analysis proceeds as follows: data for the parameters mentioned above were first collected and categorized [23-26]. The data were then fitted to an appropriate distribution. Several candidate distributions were considered: Normal, Lognormal, Exponential, Chi-Square, Cauchy, Laplace, and Logistic. The best fit distributions were determined from the Anderson-Darling goodness-of-fit test [27]. In some cases, the best fit distributions were adjusted to account for differences in the expected mean value, variance, or distribution type. For example, the mean of feedstock price was shifted from $25.4/dry ton from the original data set to $80/dry ton in order to account for additional costs associated with transportation, handling, and grower payments. Data sets with 10,000 unique samples were gathered from the best fit probability distributions.

The parameters investigated in this analysis can be divided into two categories. The first category includes all parameters except for reaction conversion factors. These parameters are incorporated directly into the financial spreadsheet to run the Monte-Carlo analysis. Reaction conversion parameters fall into the second category, whose impact on the final MFSP is evaluated indirectly via the biofuel production rate. That is, a relationship between the biofuel production rate and reaction conversions was first determined through a reduced order model of the CHEMCAD process model. A predetermined triangular distribution was assigned to the conversion of each alcohol synthesis reaction and olefin oligomerization reaction. Since a series of reactors was used for both mixed alcohol synthesis and olefin oligomerization, correlation analysis was conducted to confirm that conversion of each reaction in each reactor is independent. For instance, the conversions of methanol synthesis in the first two reactors of mixed alcohol synthesis reactors were varied simultaneously. The results indicated for each value of the conversion in the first reactor, the gap of product fuel yield between different conversions in the second reactor was almost constant (within 1% difference) and vice versa, demonstrating that the conversions of reactions in the first and second reactors are independent. Therefore it was assumed that conversions in the series of reactors were independent. After that, 21 data points were then generated for the conversion of each reaction. The built-in CHEMCAD sensitivity analysis tool was then used to investigate the impact of each conversion yield factor on the diesel biofuel production rate. The sensitivity analysis data was employed to develop a linear regression, and it was determined that alcohol and hydrocarbon synthesis yields had a linear relationship with biofuel production. Finally, all these data sets were used to obtain the ultimate linear equation between product fuel production rate and all the conversion factors. This linear equation was then used to determine 10,000 product fuel production rate data samples given the generated random data for the conversion yields. The results of the fuel production rate data, along with other key parameters were integrated into financial spreadsheets to calculate the minimum fuel-selling price (MFSP) of biofuels. With this approach, 10,000 financial iterations were run. MathematicaTM was employed to analyze the results and conduct the uncertainty analysis. Uncertainty analysis results are reported as error bars and distributions of the MFSP, and the relative impacts of the key input parameters. Figure 15 shows a flowchart of the research methodology.

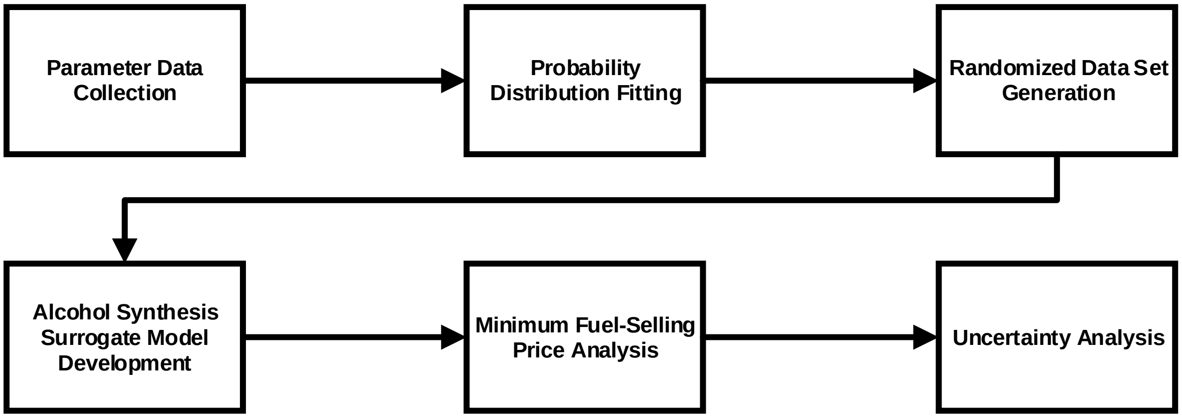

Figure 15 Flowchart of the uncertainty methodology for biomass gasification and mixed alcohol synthesis.

Historical price data for feedstock and various fuels from 2007 to 2012 were collected from several sources. U.S. average wholesale prices for gasoline and diesel and industrial natural gas and electricity prices were taken from Energy Information Administration (EIA) [24]. Feedstock price data were collected from pine pulpwood prices from the Texas A&M Forestry Service [23].

The parameters investigated in this analysis are shown in Table 4. The mixed alcohol synthesis reactor conversions shown in Table 4 were taken from the data given in [25]. Uncertainties of several parameters such as Lang Factor and catalysts costs were only investigated in the target scenario to see how they affect the MFSP. Oligomerization conversion yields differ as well based on the assumption of improving ethanol yields.

Table 4 Mean, 10% and 90% confidence levels, and best-fit distributions of selected techno-economic analysis parameters.

Parameter	Mean	10% Confidence / Min[a]	90% Confidence / Max[a]	Distribution
Industrial Natural Gas Price ($/mcf)	6.24	3.93	8.95	Lognormal
Industrial Electricity Price (¢/kwh)	6.05	5.00	7.09	Normal
Pine pulpwood ($/MT)	78.69	67.21	90.18	Lognormal
Gasoline Wholesale ($/gallon)	1.78	0.89	2.89	Lognormal
Diesel Wholesale ($/gallon)	1.76	0.59	2.92	Lognormal
Gasifier uninstalled capex (MM$)	9.80	7.35	12.93	Triangular
Tar reformer uninstalled capex (MM$)	4.90	4.90	9.70	Triangular
Installation factor	2.31	1.50	2.80	Triangular
Methanol to Ethanol Conv. Frac	0.44	0.46	0.48	Triangular
CO to Methanol Conv. Frac.	0.059	0.062	0.065	Triangular
CO to Ethanol Conv. Frac.	0.040	0.042	0.044	Triangular
CO to N-Propanol Conv. Frac.	0.015	0.016	0.016	Triangular
CO to Methane Conv. Frac.	0.039	0.042	0.044	Triangular
CO to Ethane Conv. Frac.	0.0029	0.0030	0.0032	Triangular
CO to Propane Conv. Frac.	0.0010	0.0011	0.0012	Triangular
Butene to Hexadecene Conv. Frac.	0.86	0.90	0.95	Triangular
Ethylene to Butene Conv. Frac.	0.10 (0.0011)[b]	0.11 (0.11)	0.12 (0.12)	Triangular
Ethylene to Hexene Conv. Frac.	NA[c] (0.0011)	NA (0.11)	NA (0.11)	Triangular
Syngas compressors capex[c]	100% (90%)	80% (50%)	140% (140%)	Triangular

Table 4 continued

Synthesis reactor capex[c]	100% (90%)	90% (50%)	140% (140%)	Triangular
Purge gas expanders capex[c]	100% (90%)	90% (50%)	140% (140%)	Triangular
acid gas system capex[c]	100% (90%)	100% (50%)	140% (140%)	Triangular
heat integration capex[c]	100% (90%)	100% (50%)	140% (140%)	Triangular
Compression duty (MW)[c]	100% (90%)	80% (50%)	100% (100%)	Triangular
Expander duty (MW)[c]	100% (90%)	50% (50%)	100% (100%)	Triangular
Alcohol to hydrocarbon fuels capex, MM$	NA (160)	NA (120)	NA (280)	Triangular
Catalysts Costs, MM$/year	NA (3.20)	NA (1.00)	NA (7.50)	Triangular
Lang Factor	NA (4.00)	NA (3.00)	NA (5.00)	Triangular

[a] For lognormal distribution, 10% / 90% confidence interval is given. For triangular distribution, minimum / maximum values are given. [b] Values in parentheses are used in the analysis of the target scenario. [c] NA: not available. [c] Values are given as percentage of the base case values.

Results and Discussion

Distribution fitting

Figure 16 shows fitted Probability Density Functions (PDF) of historical feedstock and energy prices. The fitted distribution for each variable is listed in Table 4. They reflect the historical trends of these commodities. Lognormal distribution best fitted historical price data for all commodities. Triangular distributions are used for variables with limited sample data.

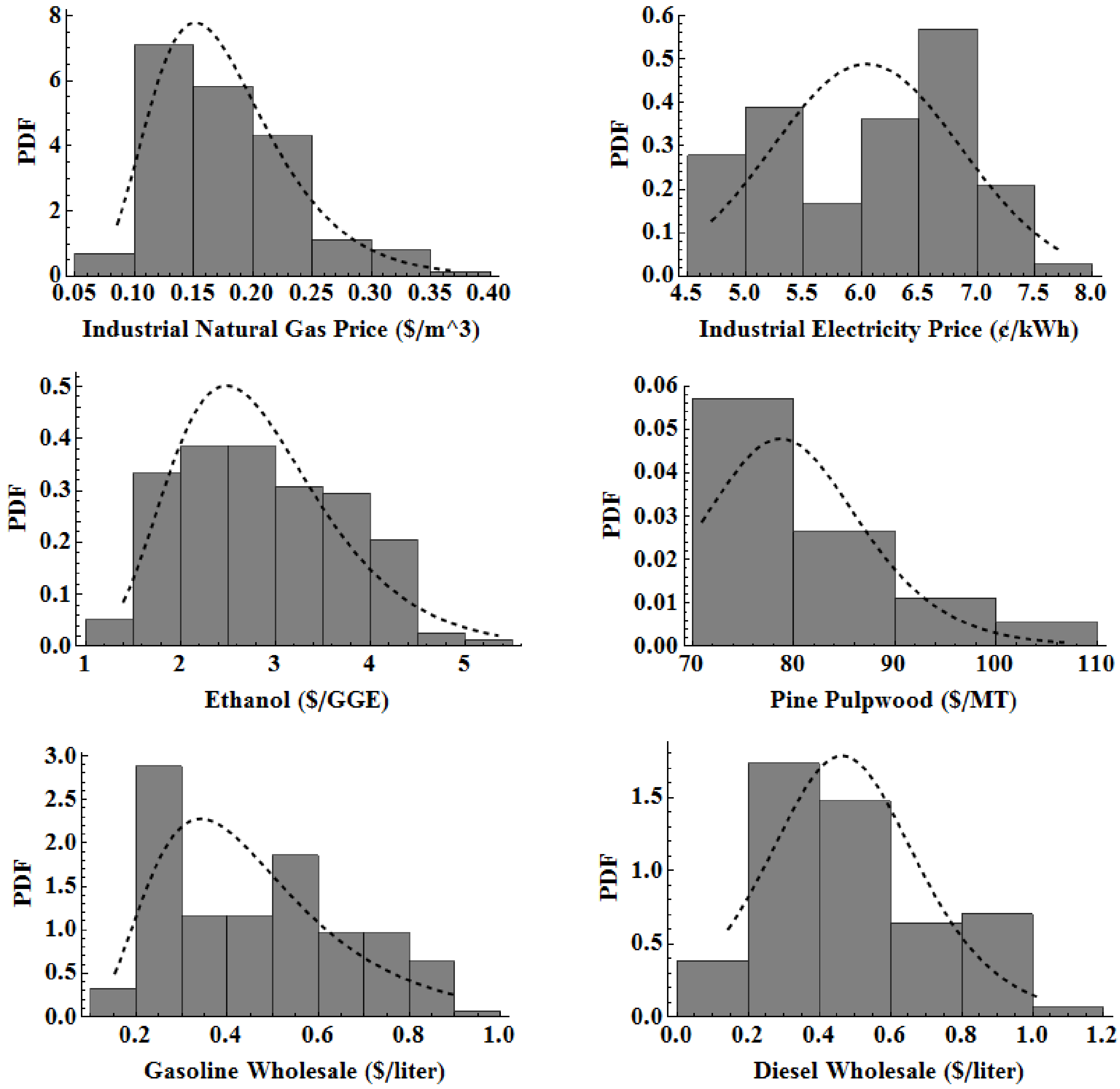

Figure 16 Fitted Probability Density Functions (PDF) of Historical Feedstock and Energy Prices.

State-of-technology scenario

Tables 5-7 show the base case results of the SOT scenario. The results are obtained by assuming the most probable values for all input variables. The estimated MFSP is high due to immaturity of some process areas such as mixed alcohol synthesis and diesel fuel production. High capital costs and heavy utility demand of these areas contribute to the high MFSP.

Table 5 Process modeling results.

Scenario	MFSP ($/L)	Fuel production rate (MM L/year)	Fuel product yield (L/dry MT feedstock)
SOT	1.79	159	246
Target	1.04	178	269

Table 6 Breakdown of Installed equipment cost in million dollars.

Scenario	Feed Handling	Gasification	Syngas Cleanup	Mixed Alcohol Synthesis	Diesel Fuel Production	Power & Heat Plant	Balance of Plant	Total
SOT	0	48.2	106.5	83.8	118.8	30.8	9.0	397.1
Target	0	48.2	83.5	58.7	59.4	27.7	9.0	286.5

Table 7 Breakdown of operating costs in million dollars.

Scenario	Feedstock	Catalysts & Chemicals	Waste Disposal	Electricity and other utilities	Fixed Costs	Capital Depreciation	Average Income Tax	Average Return on Investment	Total
SOT	57.9	19.8	0.7	11.6	44.6	47.4	25.4	79.3	286.7
Target	57.9	5.4	0.7	2.4	28.5	27.3	14.8	46.3	183.3

Figure 17 shows the probability and cumulative MFSP distributions for the high Lang Factor syngas to distillates case scenario. It can be seen that the base case MFSP lies on the left of the most probable region. The most probable MFSP value is slightly higher than the base case value. There is an 80% probability that the MFSP falls between $6.39/gal and $7.66/gal.

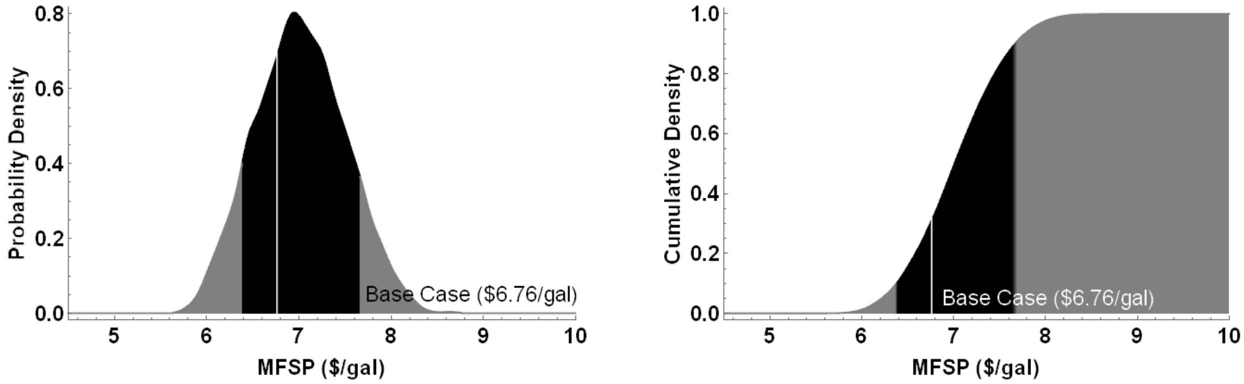

Figure 17 Minimum Fuel-Selling Price (MFSP) probability (left) and cumulative (right) distributions for syngas to distillates with high Lang factor.

Figure 18 shows the parameter uncertainty impact on the syngas to distillate MFSP for the state-of-technology scenario. This figure is more informative than traditional sensitivity analysis. It gives not only the the range of the MFSP, but also the 0.25/0.75 quartile values for each parameter investigated. In some cases, the parameter that generates the largest MFSP range does not necessarily give the largest range of 0.25/0.75 quartile values, as will be shown later in Figure 20. Figure 18 also provides the median value for each parameter in contrast to the sensitivity analysis in which only the base case value is provided for each parameter. For instance, the median value of feedstock price in Figure 18 is skewed leftward, indicating that the uncertainty of feedstock price is likely to result in a lower MFSP than the base case. Figure 18 presents the parameters investigated in such a way that the parameter with the greatest direct influence (a larger value of the parameter generates a higher MFSP) comes first while those with the greatest inverse influence (a larger value of the parameter generates a lower MFSP) come last. For example, feedstock has a positive influence on the MFSP since higher feedstock price would increase the MFSP. In contrast, higher gas hourly space velocity reduces the size of the reactors and thus capital cost; therefore it has an inverse influence on the MFSP. As is shown in Figure 18, IRR has the most significant impact on MFSP, followed by feedstock price. However, the latter has a smaller range of expected (0.25/0.75 quartile) values. This result agrees with other research regarding biomass gasification and methanol-to-gasoline [28]. The relatively low impact of process parameters, installation factors and equipment costs indicates that this process is mature.

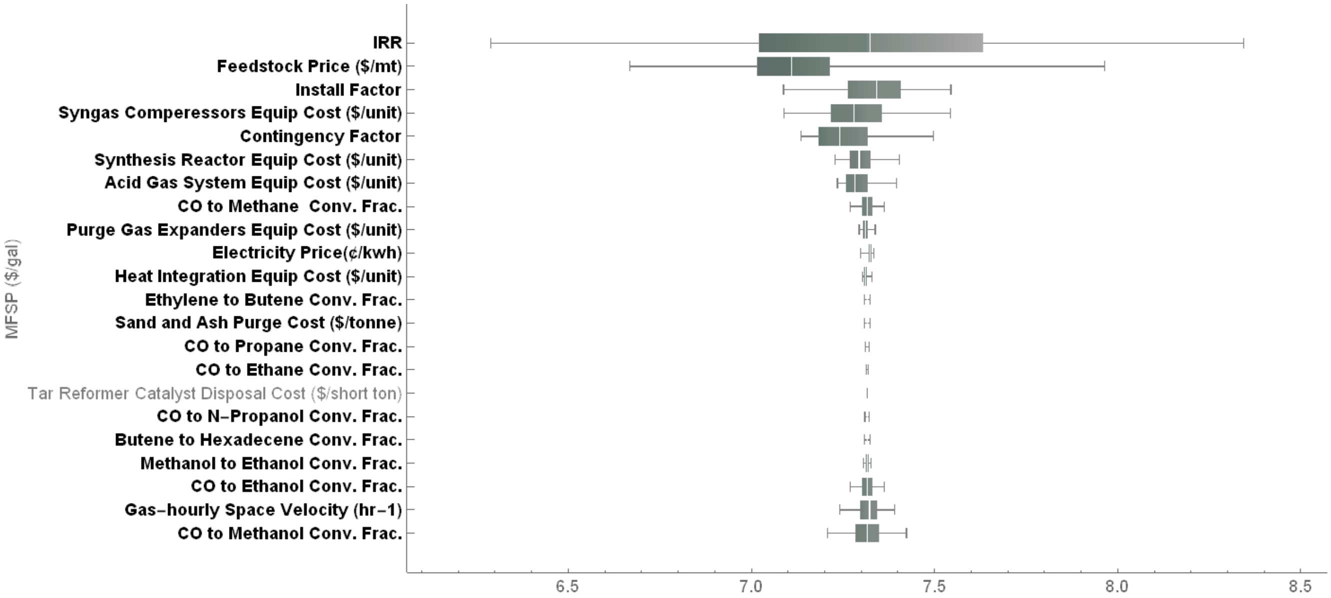

Figure 18 Syngas to distillates high Lang factor parameter uncertainty impact on the MFSP. Gates indicate min/max MFSP range; boxes indicate 0.25-0.75 quantiles of the MFSP; white vertical lines show the median MFSP value. Bold legends indicate significant ($p<0.05$) parameters.

Target Scenario

Base case results of the target scenario are shown in Tables 5-7. The main difference from the SOT scenario is that installed equipment costs related to mixed alcohol synthesis, and fuel production are lower due to improved maturity of the target scenario concept design. Installed equipment costs of steam plant are also reduced to account for lower energy demand in the target scenario. Other improvements include higher product yield and lower catalyst load in mixed alcohol synthesis, alcohol dehydration, and alkene hydrogenation reactions.

Figure 19 shows the target scenario MFSP distribution. In the target scenario, the uncertainty of Lang Factor impact was also investigated. It can be seen from Figure 19 that the base case MFSP lies on the left half of the probability density curve, while the most probable value for MFSP (~$4.25/gal) is actually higher than the base case value of $3.93/gal, indicating that there is good probability that the MFSP is underestimated. It is shown in Figure 19 that there is 80% probability that the MFSP lies between $3.81/gal and $4.89/gal.

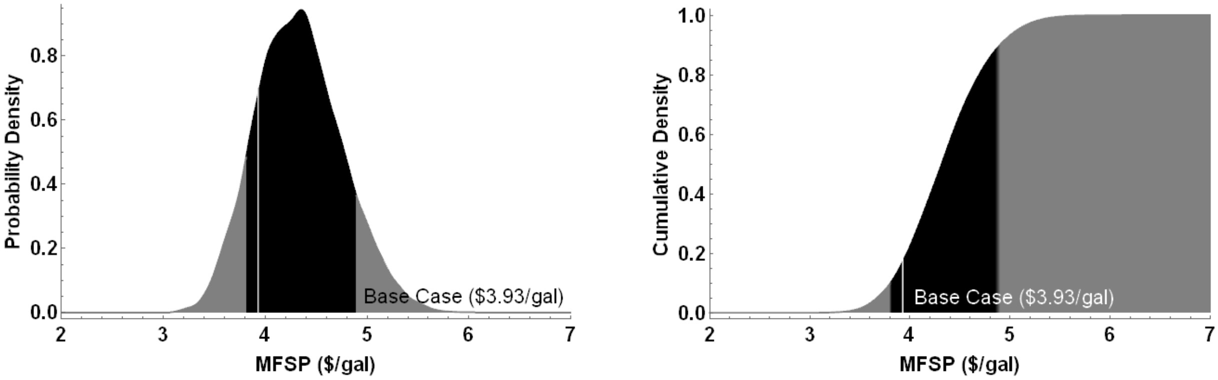

Figure 19 Minimum Fuel-Selling Price (MFSP) probability (left) and cumulative (right) distributions for syngas to distillates with low Lang factor target scenario.

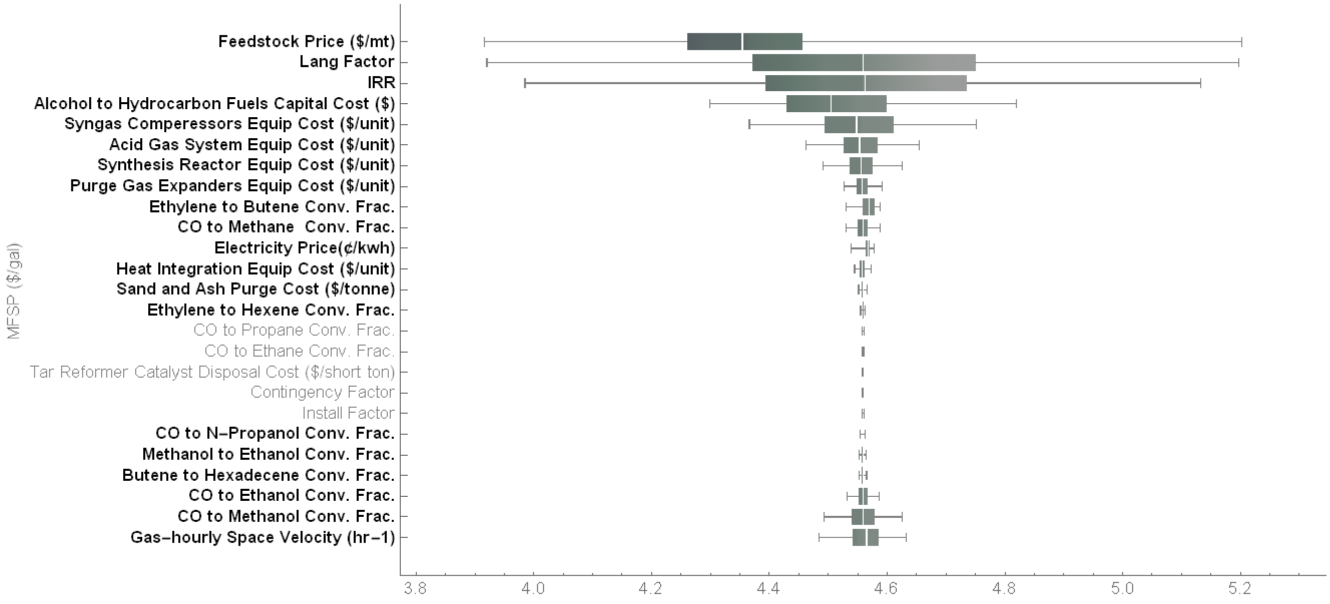

Figure 20 Syngas to distillates target scenario with low Lang factor parameter uncertainty impact on the MFSP. Gates indicate min/max MFSP range; boxes indicate 0.25-0.75 quantiles of the MFSP; white vertical lines show the median MFSP value. Bold legends indicate significant ($p<0.05$) parameters.

Figure 20 shows the impactful parameters for the target scenario. Feedstock price has the widest range of MFSP suggesting it might have the greatest impact on MFSP. However, the range of most probable feedstock prices lying between the 0.25-0.75 quantiles suggest it has a smaller influence than Lang factor and IRR. This result highlights how uncertainty analysis can enhance sensitivity analysis by identifying not only potential values but also their likelihood.

Comparison of state-of-technology and target scenarios

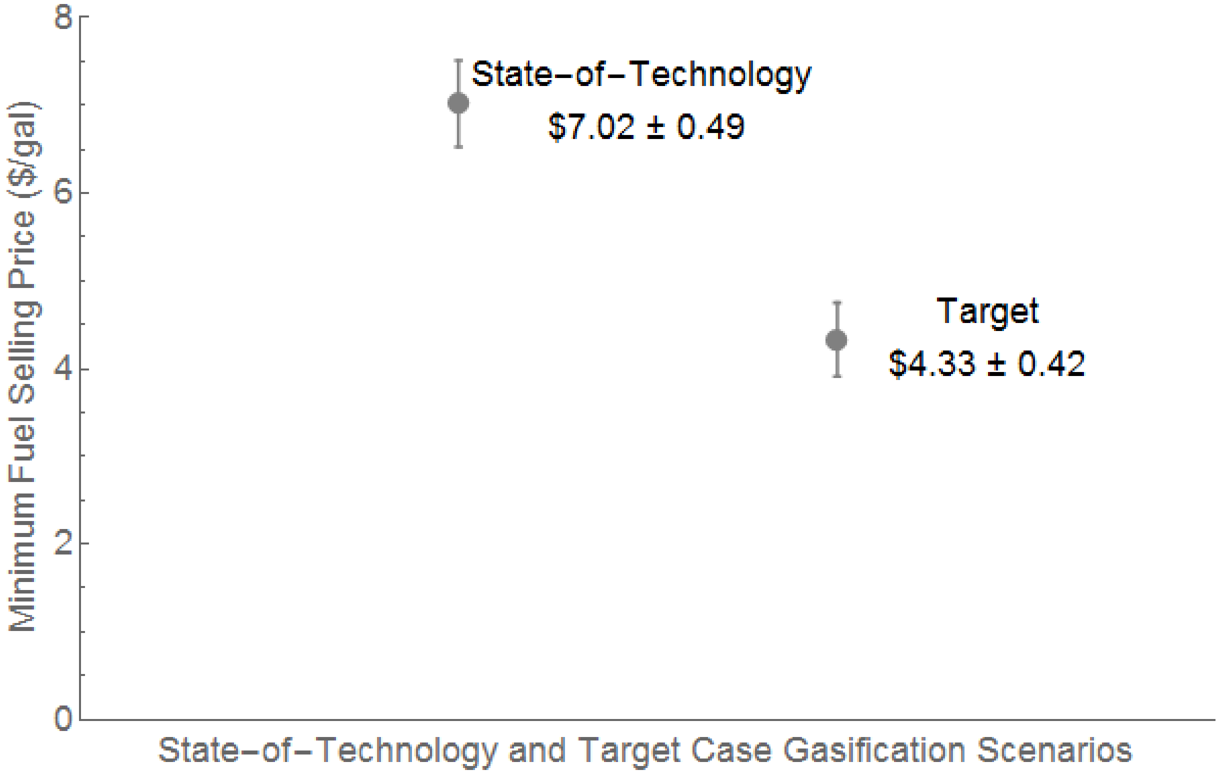

Figure 21 Syngas to distillates target scenario with low Lang factor parameter.

Figure 21 shows comparison of the two scenarios. The results indicate that the state-of-technology scenario has a high expected MFSP of $7.02 per gallon. With the capital cost being lowered in the target scenario, a lower mean MFSP ($4.33 per gallon) was obtained. Capital costs are the main contributing factors to the higher cost for the base case scenario. However, with uncertainty of more parameters being investigated, the standard deviation of the target scenario (10% of the mean MFSP) is higher than that of the state-of-technology scenario (7% of the mean MFSP).

Conclusions

This analysis investigated the uncertainty of biomass gasification and subsequent diesel fuel production process by comparing between a state-of-technology and a target scenario. Impacts of more than ten parameters on the MFSP were explored by Monte-Carlo simulation consisting of 10,000 runs. The state-of-technology scenario yielded a MFSP of $7.02/gal with a standard deviation of 0.49; the target scenario presented a MFSP of $4.33/gal with a standard deviation of 0.42. The analysis gives a 10% to 90% probability interval of the two scenarios of $6.39/gal to $7.66/gal, and $3.81/gal to $4.89 respectively.

Feedstock price and IRR were the most impactful parameters on the MFSP in both scenarios. Uncertainty of Lang Factor was investigated in the target scenario. The results indicated that it had significant impact on the MFSP. The results of this analysis justified the need to better understand uncertainties of these parameters.

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CHAPTER 4. GENERAL CONCLUSIONS

The uncertainty analysis used a Monte Carlo simulation to enable simultaneous analysis of the variability in multiple sensitivity parameters at the same time. It can also provide the extent of the error bars around the minimum fuel selling price (MFSP) estimate. The impact of parameter uncertainties on biofuel MFSP estimates in different scenarios are investigated by employing best-fit distribution and Monte Carlo methods. VBA and CHEMCAD^{TM} interfaces are used to simulate the biomass pretreatment, biomass catalytic pyrolysis/biomass gasification, biofuel upgrading process and cogeneration process. Probability distributions for the MFSP and significance levels for simulations parameters are determined and investigated.

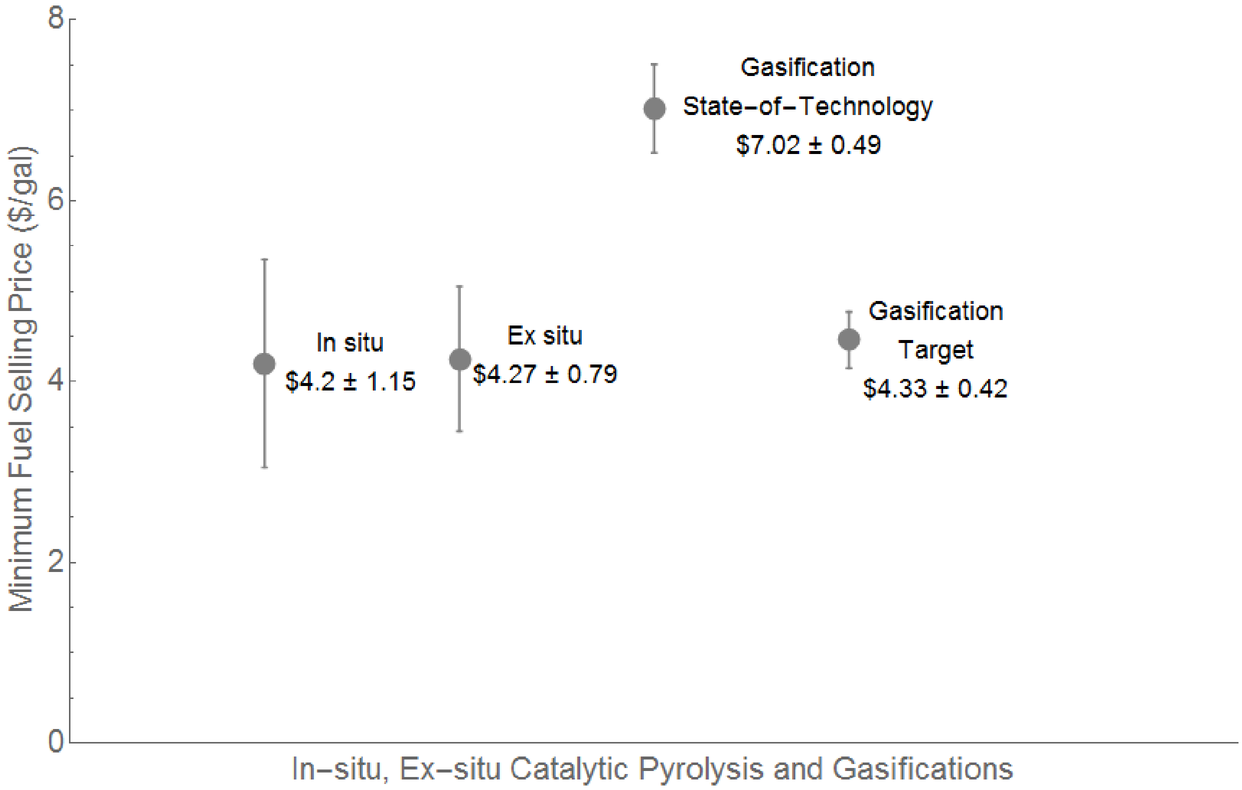

Figure 22 Minimum Fuel-Selling Price estimates and 1 standard deviation error ranges for biofuel production pathways (*In situ*, *Ex situ* catalytic pyrolysis, and gasification state-of-technology case and target case).

This study compared the MFSP uncertainty of four biofuel pathway scenarios: *in situ* and *ex situ* catalytic pyrolysis, and gasification state-of-technology case and target case. Figure 22 compares the estimated MFSP and error ranges for each scenario. The results indicate that *in situ*, *ex situ* and target gasification scenarios have similar estimated MFSP, while the MFSP for state-of-technology case is significantly higher. It also indicates the relatively low error range for gasification scenarios which is caused in part by the technical maturity of the syngas production and cleanup processes.

Sensitivity and uncertainty analyses indicate that internal rate of return and feedstock price have significant impact on MFSP across all four scenarios.

APPENDIX. ADDITIONAL MATERIAL

Table 8 Base case results for state-of-technology gasification scenario.

Minimum fuel selling price ($/gal)		$6.76	per Gallon	
Fuel production rate		42	Million Gallons per Year	
Fuel product yield		65	Gallons per Dry Metric Ton Feedstock	
Capital Costs			**Operating Costs ($/gal product)**	
Feed Handling [a]	$0		Feedstock	1.37
Gasification	$48,200,000		Catalysts & Chemicals	0.47
Syngas Cleanup	$106,500,000		Waste Disposal	0.02
Mixed Alcohol Synthesis	$83,800,000		Electricity and other utilities	0.27
Diesel Fuel Production	$118,800,000		Fixed Costs	1.05
Steam Plant & Power Gen	$30,800,000		Capital Depreciation	1.12
Balance of Plant	$9,000,000		Average Income Tax	0.60
Total Installed Equipment Cost	$397,100,000		Average Return on Investment	1.87
			Operating Costs ($/year)	
Land	$1,600,000		Feedstock	$57,900,000
Site Development	$42,872,452		Catalysts & Chemicals	19,800,000
Indirect Costs	$357,300,000		Waste Disposal	$700,000
			Electricity and other utilities	$11,600,000
Fixed Capital Investment (FCI)	$948,100,000		Fixed Costs	$44,600,000
Working capital	$47,300,000		Capital Depreciation	$47,400,000
Total Capital Investment (TCI)	$995,500,000		Average Income Tax	$25,400,000
			Average Return on Investment	$79,300,000

[a] Capital costs of feedstock handling cost is included in feedstock cost.

Table 9 Base case results for target gasification scenario.

Minimum fuel selling price ($/gal)		$3.93	per Gallon	
Fuel production rate		47	Million Gallons per Year	
Fuel product yield		71	Gallons per Dry Metric Ton Feedstock	
Capital Costs			**Operating Costs ($/gal product)**	
Feed Handling [a]	$0		Feedstock	1.24
Gasification	$48,200,000		Catalysts & Chemicals	0.12
Syngas Cleanup	$83,500,000		Waste Disposal	0.02
Mixed Alcohol Synthesis	$58,700,000		Electricity and other utilities	0.05
Diesel Fuel Production	$59,400,000		Fixed Costs	0.61
Steam Plant & Power Gen	$27,700,000		Capital Depreciation	0.59
Balance of Plant	$9,000,000		Average Income Tax	0.32
Total Installed Equipment Cost	$286,500,000		Average Return on Investment	0.99
			Operating Costs ($/year)	
Land	$1,600,000		Feedstock	$57,900,000
Site Development	$30,000,000		Catalysts & Chemicals	$5,400,000
Indirect Costs	$143,200,000		Waste Disposal	$700,000
			Electricity and other utilities	$2,400,000
Fixed Capital Investment (FCI)	$545,500,000		Fixed Costs	$28,500,000
Working capital	$27,200,000		Capital Depreciation	$27,300,000
Total Capital Investment (TCI)	$572,700,000		Average Income Tax	$14,800,000
			Average Return on Investment	$46,300,000

[a] Capital costs of feedstock handling cost is included in feedstock cost.

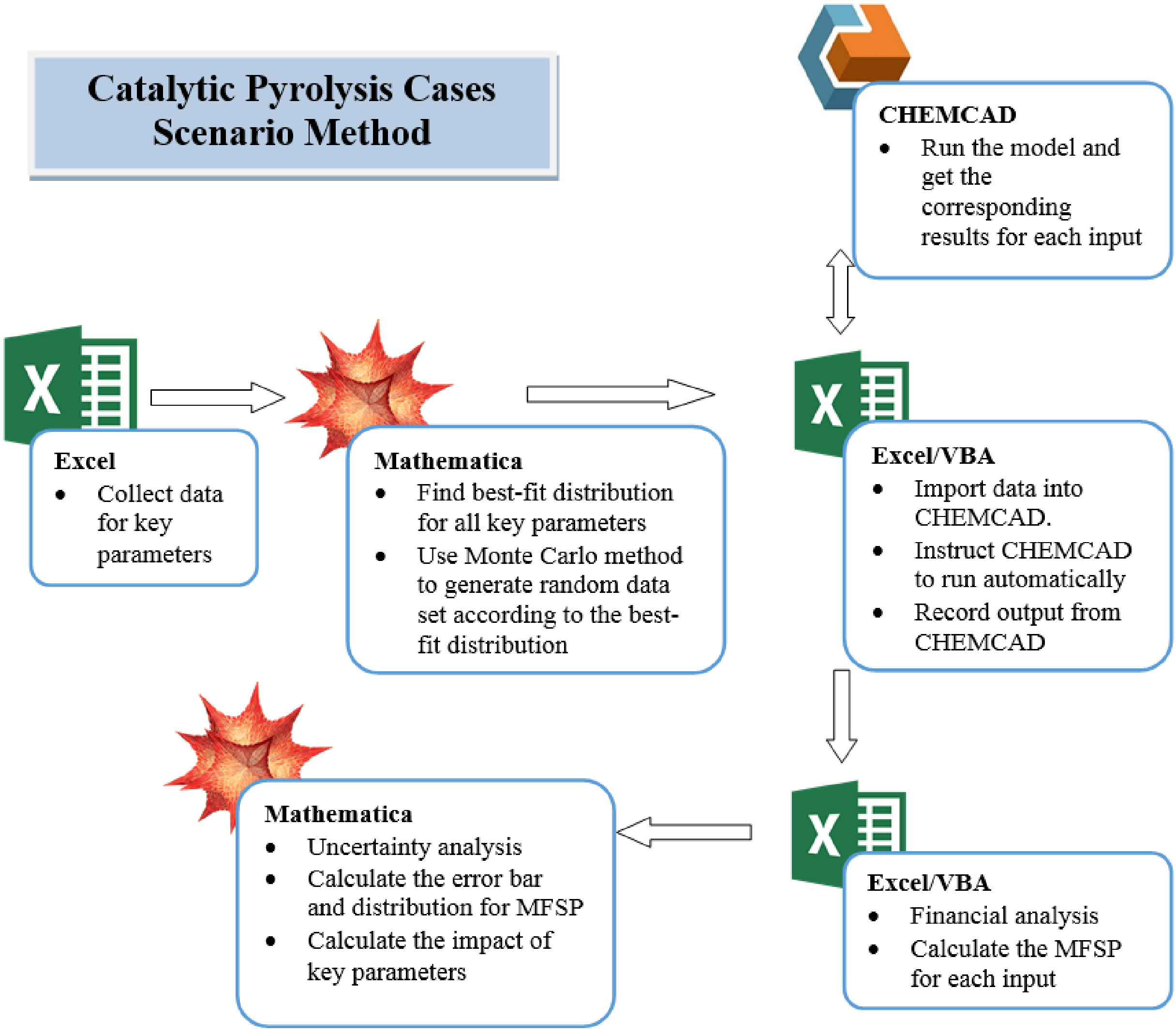

Figure 23 Flowchart description of the uncertainty analysis methodology for catalytic pyrolysis scenarios.

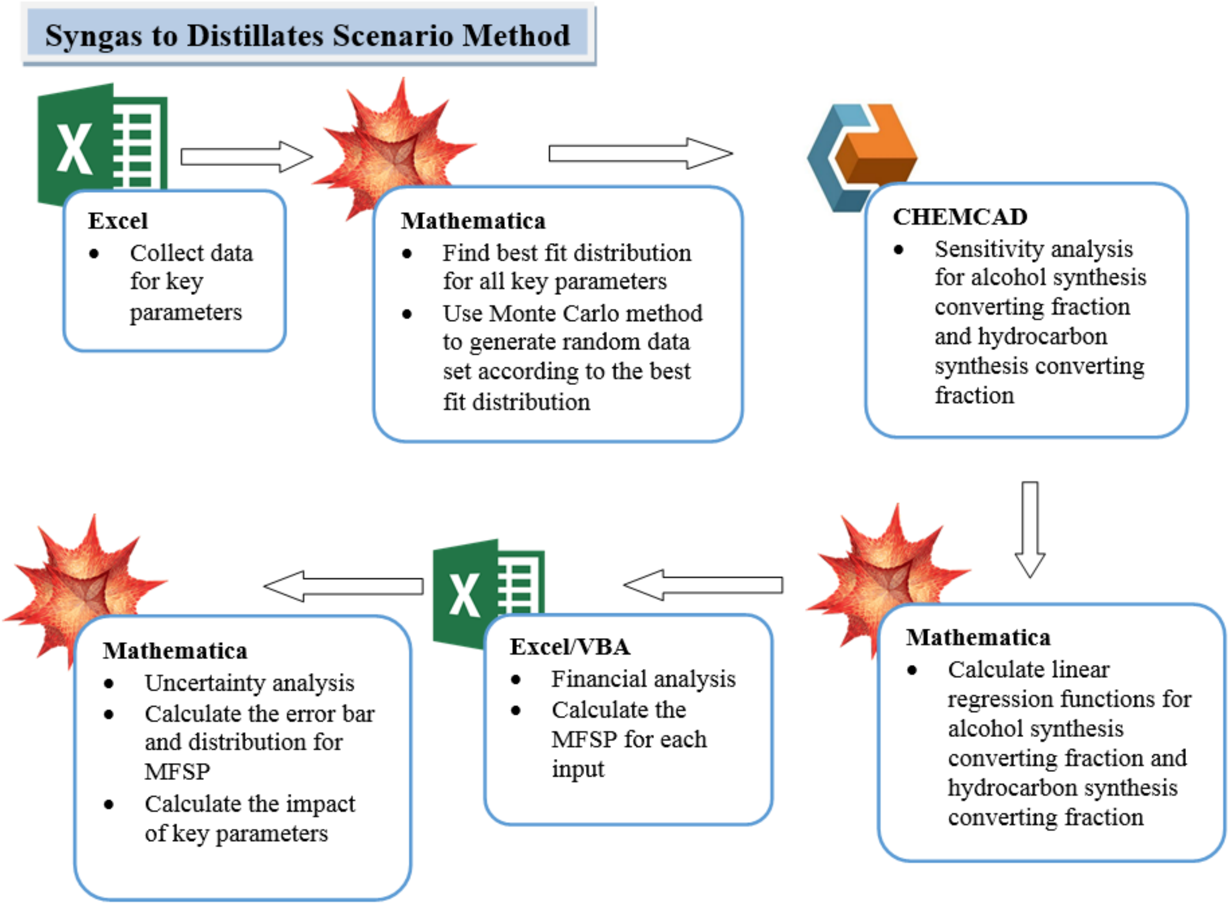

Figure 24 Flowchart of uncertainty analysis methodology for gasification scenarios.

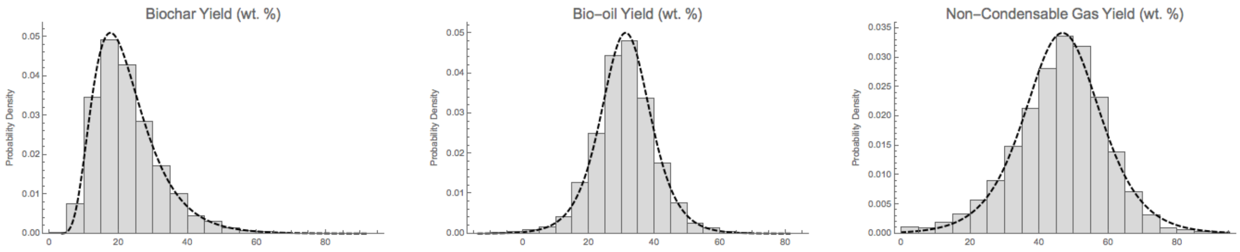

Figure 25 *Ex situ* catalytic pyrolysis biochar, bio-oil, and non-condensable gas yields based on *in situ* experimental data.

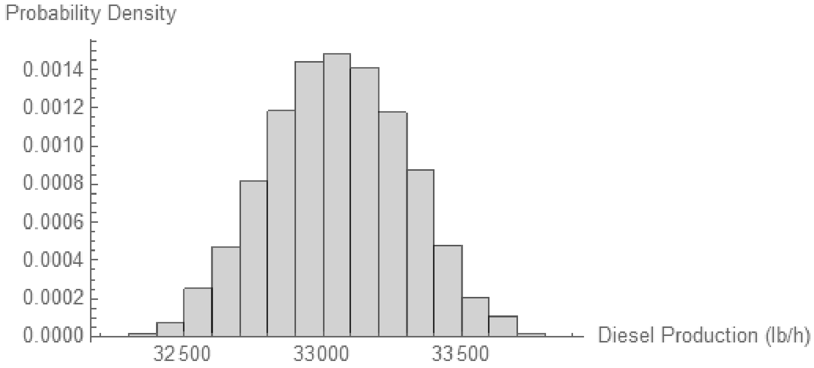

Figure 26 Diesel production probability distribution for syngas to distillates case scenarios.

Table 10 Syngas to distillates capital expenses ranges for the gasifier and tar reformer for both state-of-technology and target gasification cases.

Gasifier			**scaled**	
MTPD dry biomass		500	1000	Assumed scalable from 500 to 1000 tpd
Cost year		2010	2010	
TPEC, mm$		9.7	14.7	Taylor biomass gasifier integrated tar cracker
Install Factor		2.31	2.31	
Total Installed		22.4	34.0	
Assumed split between gasifier and tar reformer				
TIC to gasifier		2/3	2/3	
TIC to tar reformer		1/3	1/3	
Gasifier uninstalled capex			9.8	
Tar reformer uninstalled capex			4.9	
CAPEX ranges:		**mm$**	**mm$**	
Gasifier + Tar Cracker		19.4	14.7	Lower: 2 @ 500tpd, Upper: 1 @ 1000tpd
Gasifier at 2/3 cost		12.9	9.8	
Tar Reformer at 1/3 cost		6.5	4.9	
Summary:	**Base**	**Min**	**Max**	
Gasifier uninstalled capex	9.8	7.35	12.93	
Gasifier uninstalled capex	100%	75%	132%	Lower: numbers up, Upper: scales up
Tar reformer uninstalled capex	4.9	4.9	9.7	
Tar reformer uninstalled capex	100%	100%	198%	Lower: base cost, Upper: half the cost
Install factor	2.31	1.5	2.8	

Table 10 continued.

Install factor	100%	65%	121%	Per Couper et al, 2nd ed

Table 11 Syngas to distillates operating expenses ranges for the gasifier and tar reformer for both state-of-technology and target gasification case.

Summary:	**Base**	**Low**	**High**
CAPEX			
Syngas compressors	100%	80%	140%
Synthesis reactor	100%	90%	140%
Purge gas expanders	100%	90%	140%
acid gas system	100%	100%	140%
heat integration	100%	100%	140%
OPEX			
Compression duty, MW	100%	80%	100%
Expander duty, MW	100%	50%	100%

Table 12 Syngas to distillates capital expenses ranges for the mixed alcohol reactor for state-of-technology gasification case.

	Parameter	**Low**	**Base**	**High**
Alcohol synthesis	**Methanol to Ethanol Conv. Frac**	0.4351	0.458	0.4809
	CO to Methanol Conv. Frac.	0.05871	0.0618	0.06489
	CO to Ethanol Conv. Frac.	0.0399	0.042	0.0441
	CO to N-Propanol Conv. Frac.	0.014915	0.0157	0.016485
	CO to Methane Conv. Frac.	0.039425	0.0415	0.043575
	CO to Ethane Conv. Frac.	0.00285	0.003	0.00315
	CO to Propane Conv. Frac.	0.001045	0.0011	0.001155
Alcohol to hydrocarbon	**Butene to Hexadecene Conv. Frac.**	0.81	0.9	0.99
	Ethylene to Butene Conv. Frac.	0.1017	0.113	0.1243

Table 13 Syngas compression operating expenses and capital expenses ranges as related to mixed alcohol operating pressure for state-of-technology gasification case.

Summary:	**Base**	**Low**	**High**
CAPEX			
Syngas compressors	100%	80%	140%
Synthesis reactor	100%	90%	140%
Purge gas expanders	100%	90%	140%
acid gas system	100%	100%	140%
heat integration	100%	100%	140%
OPEX			
Compression duty, MW	100%	80%	100%
Expander duty, MW	100%	50%	100%

Table 14 Syngas compression operating expenses and capital expenses ranges as related to mixed alcohol operating pressure for target gasification case.

	Base	**Low**	**High**
CAPEX			
Syngas compressors	90%	50%	140%
Synthesis reactor	90%	50%	140%
Purge gas expanders	90%	50%	140%
acid gas system	90%	50%	140%
heat integration	90%	50%	140%
OPEX			
Compression duty, MW	90%	50%	100%
Expander duty, MW	90%	50%	100%
CAPEX			
Alcohol to hydrocarbon fuels, mm$	160	120	280
OPEX			
Catalysts Costs, mm$/year	3.2	1.0	7.5
Lang Factor	4	3	5

Table 15 Mixed alcohol reactor performance assumptions for target gasification case.

	Parameter	Low	Base	High
Alcohol synthesis	**Methanol to Ethanol Conv. Frac**	0.4351	0.458	0.4809
	CO to Methanol Conv. Frac.	0.05871	0.0618	0.06489
	CO to Ethanol Conv. Frac.	0.0399	0.042	0.0441
	CO to N-Propanol Conv. Frac.	0.014915	0.0157	0.016485
	CO to Methane Conv. Frac.	0.039425	0.0415	0.043575
	CO to Ethane Conv. Frac.	0.00285	0.003	0.00315
	CO to Propane Conv. Frac.	0.001045	0.0011	0.001155
Alcohol to hydrocarbon	**Butene to Hexadecene Conv. Frac.**	0.81	0.9	0.99
	Ethylene to Butene Conv. Frac.	0.00113	0.113	0.11865
	Ethylene to Hexene Conv. Frac.	0.00109	0.109	0.11445

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