

INTEGRATION OF DECENTRALIZED BIOMASS UPGRADING DEPOTS AND
CENTRALIZED CATALYSIS TO MAKE GREEN AROMATICS

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ABSTRACT

INTEGRATION OF DECENTRALIZED BIOMASS UPGRADING DEPOTS AND CENTRALIZED CATALYSIS TO MAKE GREEN AROMATICS

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Monoaromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylenes (BTEX), are widely used as additives to gasoline and precursors to polymers. Green aromatics from renewable biomass, as a substitute for aromatics from petroleum refining, are essential for reducing worldwide dependence on petroleum and carbon dioxide emissions. Catalytic fast pyrolysis of biomass potentially offers a green route to make BTEX. However, biomass' high oxygen content is unfavorable for making aromatics as it reduces the efficiencies of transport and conversion. Furthermore, the low bulk density of biomass results in a high transport cost. Biomass upgrading technologies, such as torrefaction, partially removes the chemically bound oxygen in biomass, thus lowering subsequent transport and conversion costs. Pelletization, after torrefaction, further lowers transport costs by increasing the bulk density of biomass.

This study investigates the integration of decentralized biomass upgrading depots with a centralized BTEX production facility. An economic analysis of this bioenergy system was conducted to examine BTEX yields, biomass costs and their sensitivities. Model predictions were verified experimentally using pyrolysis GC/MS to quantify BTEX yields for raw and torrefied biomass. A group of factors, including torrefaction temperature, residence time, upgrading depot capacity and biomass on-site drying time, were optimized using the minimum production cost as the objective function. This optimization study found conditions that justify torrefaction as a pretreatment for making

BTEX provided that starting feedstock costs are below \$58 per tonne.

Dedicated to my family.

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Chapter 1 Introduction

Biomass is as an important potential source to renewable energy and green chemicals. Converting biomass into green fuels and chemicals via biological or chemical method is being studied widely. Aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylenes (BTEX) are important intermediates for the production of polymers and can be used as fuel additives. Production of aromatics from lignocellulosic biomass is commonly performed by a combination of pyrolysis and catalysis. Compared to fermentation, pyrolysis is less expensive, easier to be scaled and more compatible with the existing hydrocarbon-based infrastructure. However, high costs of biomass feedstock in collection, transport, handling, and storage limit green chemicals to being commercialized.

Biomass upgrading depots (BUDs), which pretreat biomass into a form with improved properties, can make biomass more easily to be transported, handled, and stored. Pelletization and torrefaction are two common pretreatment technologies. Pelletization increases bulk physical density of biomass from a range of 60 to 250 kg/m³, to a range from 360 to 650 kg/m³ [1]. A high bulk density saves costs of transport and storage. Torrefied biomass has improved properties such as hydrophobicity and imperishability [2, 3]. Torrefied biomass also has a higher energy density, which benefits the bioenergy production, and a lower oxygen content, which benefits the aromatics production [4]. By building several BUDs to serve a central biorefinery, supply chain system benefits from lower cost, reduced risk, and better product quality.

The goal of this dissertation is to design a supply chain system that integrates BUDs with a central biorefinery to produce green aromatics from biomass. This supply

chain system will allow a large size of biorefinery, and will reduce the production cost for the areas where biomass is hardly collected and transported. The objectives of this dissertation are as follows:

- Analyzing economics of biomass upgrading depots and BTEX production
- Examine aromatics production from torrefied biomass
- Optimizing process variables to lower the BTEX production cost

In chapter 3 of this dissertation, we formulated a model to estimate the economics of biomass upgrading depots (BUDs). Process variables including capacity size and biomass on-site drying time were optimized to minimize the production cost of BUDs. The suitable selections of pre-treatment technologies in BUDs were determined at different hauling distances and weather conditions. To justify the enhancement of torrefaction on BTEX production, TGA and pyrolysis GC/MS were employed perform experiments. The mass and energy balance data were collected and integrated into the economic model developed in chapter 4. In chapter 5, the study was expanded to build regression models to predict the torrefaction mass yield and BTEX yields as functions of torrefaction severity. These prediction models enabled us to optimize process conditions. Finally, the feasibility of integrating BUDs with a centralized BTEX production facility was studied.

Chapter 2 Literature Review

2.1. Biomass Upgrading Depots (BUD)

Biomass has been being considered as an alternative to produce renewable energy and green chemicals. However, a series of characteristics of biomass constrain bio-refinery facilities to be commercialized: low density and high moisture content make delivery cost intensive; hydrophilic and biodegradable cause unforeseen storage problems [3]; arriving in various forms and types results in highly heterogeneous [5]; dispersed distribution and low yield per unit area give rise to a large collection radius [6]. By building several biomass pre-treatment conversion depots to serve a central bio-refinery, supply chain system can receive benefits in aspects of cost, risk, and product quality.

2.1.1. Densification

Densification process makes biomass feedstock easier to be handled, stored, and transported. Pelletization is the most common densification technology for biomass [2]. Pelletization can increase the bulk density from 60 to 250 kg/m³ for biomass up to from 360 to 650 kg/m³ for pellets [1]. Pelletization is usually carried out by pelletizers. The main components of a pelletizer contain a ring die with holes through it, and one to three rotating rolls. The process during pelletization is as follows: biomass feedstock enters into the inside of ring die; and then rotating rolls press the biomass through holes from inside to outside; and finally pelletized biomass coming through the ring die is cut by a knife into the desired dimension size [7].

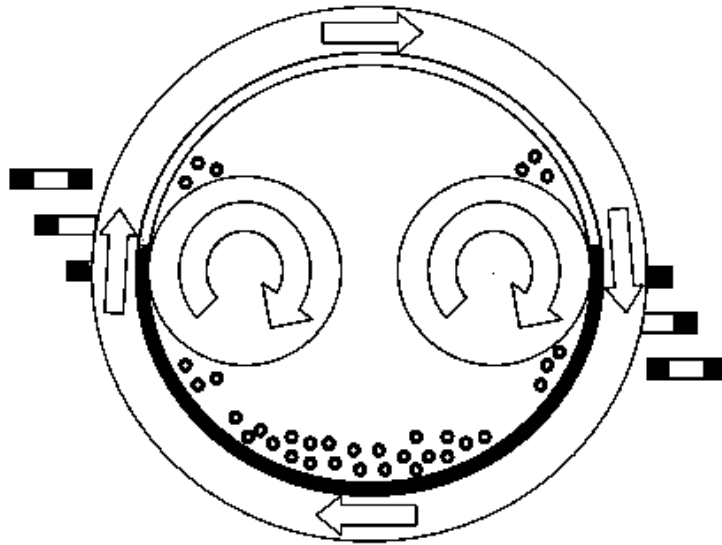


Figure 2.1.Schematic of ring-die pelletizers [7]

Mani et al. estimated the capital investment of pelleting plant to be at 2.2M\$ (in 2004 USD) for a capacity of 6 tons per hour [8]. The production cost could drop from \$51 per tonne down to \$40 per tonne when the capacity increased to 10t/hour. The fact that the economies of scale can significantly reduce production costs was also proven by other researchers [9]. Thek and Obernberger investigated the economics of pellets production under Australia conditions, and reported that pellets production cost is higher by 25€/t than in Sweden because larger scale units and high efficiency heat recovery system are applied in Sweden [9]. They also indicated that the main components of production costs include biomass material, personnel, drying, and pelletization. Tripathi et al. built a series of statistical models to estimate the cost functions such as capital costs, maintenance costs, and energy costs [10]. The authors indicated that an appropriate and opportune maintenance is essential to ensure densification equipments running well. They constructed a very detailed maintenance model on daily, weekly, monthly, and six-

monthly basis to estimate maintenance cost function.

2.1.2. Torrefaction

Torrefaction is a preprocessing technology that upgrades biomass to a form with improved physical and chemical properties. In torrefaction, heat is added in the absence of oxygen to perform a mild pyrolysis of the structural components of biomass. Operating conditions include temperatures ranging from 200 °C to 400 °C and residence times from 5 to 60 minutes. Generally, 70% of the starting mass is retained in the torrefied wood, and this product contains 90% of the energy because a large amount of oxygen is liberated as water and carbon oxides in the product gas[11, 12]. Heat required by the torrefaction reactor can be supplied by combusting this gas if autothermal operation can be achieved [13].

Torrefaction cost is hard to be estimated, since there is no available commercially proven torrefaction plant. Bergman et al. and Uslu et al. estimated costs of a torrefaction production line with capacity of 60kton per year [11-13]. Capital investments are between 5.2M€ and 7.5M€ (in 2004 index), and production costs range from €40 to €56 per ton. Equipment costs and installation costs are 31% and 39% of the total fixed costs, respectively. Torrefaction costs depend on torrefaction technologies. Bergman et al. compared three different torrefaction technologies, and stated that moving bed reactor is the most economical attractive technology [13]. The reason is that moving bed reactor has 100% fill percentage, which results in small volume, and high heat transfer rate, which requires low resident time. Bergman et al. also provided that the maximum capacity of a single moving bed reactor is 30kton per year, and the capital investment of that is 275k€. Shah et al. suggested a capital investment of 7.5M\$ for the torrefaction

plant capable of 25 tons of product per hour [14]. With an operating period of 6 months per year, and 20% of the designed operating time for maintenance, the production cost excluding feedstock cost was estimated to be \$17.5 per ton of product.

2.1.3. Combination of torrefaction with densification

After torrefaction, biomass becomes porous and fragile, which result in a low density and a low durability. It is a big challenge to transport and handle such a material. Combining densification is considered as a good solution to deal with this problem. Additionally, torrefaction also can improve the quality of densified biomass.

Koukios G.E. suggested to improve product properties by heating biomass during densification [15]. It is believed that the fragile property of torrefied biomass can save by up to 90% of energy consumption during size reduction [16, 17]. Thus, Bergman combined torrefaction with densification in two steps rather than one step, by adding torrefaction after drying and before size reduction [12]. Bergman compared two scenarios: conventional pelletization process (CP) and combined torrefaction with pelletization process (TOP) [12]. TOP process has the higher capital investment due to the addition of torrefaciton process, but there is a significant drop in the energy cost for TOP. This is due to the reduction of natural gas usage and grinding energy requirement during the TOP operation. When feedstock consumption and equipment depreciation are accounted, the total production cost of TOP process becomes a little higher than CP process [18, 19]. However, a long distance transport can bring TOP process to a more economical level than CP process [20].

2.1.4. Properties of torrefied and densified biomass

Making appropriate assumptions and deriving proper functions for properties of

pre-treated biomass are essential for developing supply chain model, since characteristics of pre-treated biomass have effects on the processes of storage, transport, and handling. Many studies have been focused on modeling and testing physical properties of torrefied pellets and conventional pellets. Hydrophobicity of a solid fuel is important as cover unites are required for those hydrophilic solid fuel during storage and transport. Medic, D. et al. compared several mathematical water absorption model for torrefied wood and untreated wood [21]. Wilén, C. et al. did hydrophobic tests for torrefied pellets and conventional pellets [22]. When being exposed to humid ambient for a long time (more than 2000 minutes), torrefied pellets have a lower equilibrium moisture content that varies from 9% to 11%, while conventional pellets range from 12% to 15%. Torrefied pellets are also prone to keep integrated in both of rain exposure and water immersion experiments. When being exposed to a warm and humid atmosphere for a period, biomass tends to be degraded by microbial. Torrefaction improves the resistance of microbial degradation significantly, which makes storage more easy [21]. Although torrefaction enhances resistances of water absorption and microbial degradation, it is still doubtful that torrefied pellets could be stored in field like coal. Ehrig, R. et al. tested the storage behavior of a pile of 4 t torrefied pellets that is from European market [18]. By being stored in field, depths of 30cm and 50cm of completely decomposed layers were found after storage periods of 1 month and 4 months, respectively. The durability of a solid means the ability to remain intact during storage and handling. Wilén, C. et al. stated that the durability of torrefied pellets is only 88%-92%, that is not at a desired level, while conventional pellets is at 98% [22]. Grinding is usually applied to feedstock prior pelletization and to solid fuel before entering some of combustion boilers. Grindability

determines the cost and energy consumption during grinding. Torrefaction has advantages of increasing grindability by up to 14% and saving grinding energy by up to 90% [16, 17].

2.2. Biomass biorefineries: converting biomass into green aromatics

2.1.1. Pyrolysis

Pyrolysis is a thermalchemical treatment that heats the biomass in the absence of oxygen. Applied operating temperature usually ranges from 500°C to 800°C [23]. The main products in the pyrolysis include non-condensable gas, char, and bio-oil. Pyrolysis could be conducted fast or slowly by adjusting heating rate and resident time. High heating rate and short resident time can minimize secondary reactions, thus a high yield of bio-oil can be achieved [24]. While slow pyrolysis is suitable to produce char, fast pyrolysis is applied to make bio-oil. It is typically required in the fast pyrolysis that heating rate is larger than 10K/s, and resident time is shorter than 10s [25].

Table 2.1 Overview of fast pyrolysis reactors [26]

Property	Status	Bio-oil (wt%)	Complexity	Feed size	Inert gas need	Specific size	Scale Up
Fluid bed	Comm	75	Medium	Small	High	Medium	Easy
CFB	Pilot	75	High	Medium	High	Large	Easy
Entrained	None	65	High	Small	High	Large	Easy
Rotating cone	Demo	70	High	V small	Low	Small	Medium
Ablative	Lab	75	High	Large	Low	Small	Hard
Vacuum	Demo	60	High	Large	Low	Large	Hard

A variety of technologies have been applied to conduct biomass fast pyrolysis (Table2.1). Fluidized beds and circulating fluidized beds (CFB) are the most common technologies because they are easy to be scaled up [26]. Nevertheless, both of these two reactors need a heating transfer medium such as sand to perform the reaction [25]. In

order to fluidize the mixture of sand and biomass, a large amount of inert gas is also required. Thus, high operating costs prevent these two reactors to be cost-efficient.

2.1.2. Green aromatics from pyrolysis vapors

Monocyclic aromatics, such as benzene, toluene, ethylbenzene and xylenes (BTEX), are important chemicals, which can be used as additives to fuels and precursors for polymers. Many researchers have demonstrated that pyrolysis vapors can be converted into aromatics [27, 28]. Zeolite catalysts such as HZSM-5 are commonly applied to convert biomass into aromatics [27, 29-31]. Kelkar investigated a variety of biomass as feedstock to produce BTEX and reported that spent coffee ground is an ideal feedstock which has a weight yield of 7% [4]. Poplar and corn stover, as the common biomass resources from forestry and agricultural, obtain BTEX yields of 3.8% and 2.1%, respectively [4]. Hilten et al. investigated the effects of torrefaction on the aromatics production [32]. The authors concluded that torrefaction has limited effects on aromatics yields, but can significantly reduce the yields of reactor char, catalysts coke and, catalysts tar.

2.3. Supply chain model design and optimization

Gold et al. stated that the key issues for the bioenergy production system are biomass transport, storage, and supply chain system design [33]. Costs and risks of the bioenergy production and supply system need to be controlled. A supply chain model is in need to help to make decisions, and to optimize a series of variables, such as facilities numbers, locations, and capacities.

Economic behaviors of bio-refinery facilities are different from that of fossil fuel based facilities [34]. With the increase of biomass-processing facility size, the capital cost per unit of product decreases due to the economies of scale. Nevertheless, a great biomass

collection area is in need for a large biomass facility, and therefore leads to a long biomass transport distance. There is a trade-off between economies of scale and economies of transportation. Thus, an optimal scale size exists for biomass processing facilities.

Jenkin built a mathematic model to determine the optimal size for biomass utilization facilities [35]. In his study, two scenarios were considered: 1) scaling factor of facility is constant; 2) scaling factor is variable and the function of capacity. Nguyen and Prince estimated the optimal capacity size for a bio-ethanol facility using mixed crops as feedstock [36]. The authors developed a simplified model in which the production cost and transport cost were represented as exponential functions. They reported that prices of crops have no effect on the optimal size, but high transport efficiency attains a large optimal capacity. This is supported by Leboreiro and Hilaly [37]. Leboreiro and Hilaly developed the biomass transport model and determined the optimal size for bio-ethanol facilities [37]. They studied the effects of transport efficiency and scaling exponent on the optimal production capacity, and reported high transport efficiency and low value of scaling exponent allow a large optimal facility size.

An appropriate location for the biomass conversion facility is essential to minimize the transport cost. A variety of methods were proposed aiming at finding the optimal facility location for a bio-refinery. Each of methods has both of limitations and superiorities. Marvin et al. compared performance of tabu search, simulating annealing and genetic algorithms on different facility location problems, and concluded that genetic algorithms outperform the other two methods in the most of situations [38]. Although genetic algorithms succeeds in solving non-linear and discrete problems and being close

to the global optimum, the running time of genetic algorithms significantly increases after several stages especially for the complex facility problems. Sequential quadratic programming is another optional optimization method to solve the facility problems. It allows an extremely fast convergence, but a local optimum may be obtained rather than the global optimum. Rentizelas and Tatsiopoulou used a hybrid optimization method, which combined genetic algorithms with sequential quadratic programming to overcome each disadvantages, to determine the optimal bioenergy facility [39]. Bowling et al. simplified the bio-refinery facility problem to be a linear problem [40]. Mixed integer linear program method was applied to develop the supply chain model, and therefore all of the functions in the model including the capital cost were linearized. The authors also considered to build hubs around the central facility in order to reduce the transport cost. The optimal facility locations were shown as points on a coordinated map in their results. In some situations, it may be unfeasible to build the facility at the optimum location. It is important to determine potential suboptimal locations for the decision making. Nanthavanij and Asadathorn presented an analytical method to construct cost contour lines in a optimum location map which help find alternative locations [41]. This method was also applied by other researchers to present the relationship of total production costs and geographic coordinates of facilities [39].

Chapter 3 Comparing Pelletization and Torrefaction Depots: Optimization of Depot Capacity and Biomass Moisture to Determine the Minimum Production Cost

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3.1. Abstract

In the present study, the biomass upgrading depot capacity and biomass feedstock moisture were optimized to obtain the minimum production cost at the depot gate for the production of woody biofuels. Three technology scenarios are considered in this study including: 1) conventional pellets (CP), 2) modestly torrefied pellets (TP1) and severely torrefied pellets (TP2). TP1 has the lowest cost of \$7.03 /GJ_{LHV} at a moisture of 33 wt.% and a depot size of 84 MW_{LHV}. The effects of weather conditions and biomass field conditions were also studied for three scenarios. In humid regions of Michigan, TP2 is more economical than other scenarios because of the increased production of combustible gas. The three scenarios have similar sensitivities to biomass field conditions.

Keywords: pelletization; torrefaction; depot scale; biomass moisture; production cost

3.2. Introduction

Renewable feedstocks and conversion strategies are needed for making solid fuels that can displace coal for heat and power production [42]. Several states within the U.S.A. have enacted renewable fuel standards that mandate a portion electrical grid energy be renewable in origin [43]. Forest biomass is an important potential source of renewable energy because of its abundance and availability. Further, woody biomass can be efficiently grown on marginal lands in plantations. Harvested biomass can be chipped and piled in the field to increase its value, however, the low bulk density and low heating

value of raw woody biomass constrains its commercial use [44]. Upgrading, either by densification or torrefaction followed by densification, is needed to improve biomass properties.

Direct biomass densification improves handling, storage and transportation characteristics. Pelletization is one of the most common densification technologies for solid fuel production [2] as it can increase the bulk density of raw biomass by up to 5 times [1]. Chen et al. stated that combustion properties of raw biomass, such as HHV and O/C ratio can be improved significantly by torrefaction [45]. Torrefaction is a preprocessing technology that typically precedes densification to improve the physicochemical properties of raw biomass [46, 47]. In torrefaction, heat is added in the absence of oxygen to perform a mild pyrolysis of the structural components of biomass [48]. Operating conditions include temperatures ranging from 200 °C to 400 °C and residence times from 5 to 60 minutes [11, 12]. Generally, 70 to 80% of the starting mass is retained in the torrefied wood, which contains up to 90% of the starting energy because bound oxygen is liberated as water and carbon oxides in the product gas [11, 12]. Heat required by the torrefaction reactor and for biomass drying can be supplied by combusting this gas, a mode known as autothermal operation when external fuel is not needed [13]. After torrefaction, biomass becomes porous and fragile, resulting in low density and low durability. As handling and transporting such a material is challenging and costly, densification typically follows torrefaction to improve bulk physical properties [12, 49].

The production of raw biomass pellets or torrefied biomass pellets, to take place in biomass processing depots, is subject to the competing effects of process scale,

transportation distance, and moisture content. The minimum production cost for 1) densified only or 2) torrefied and densified fuels is a strong function of depot capacity and feedstock moisture content. It is important to note that the economic behavior of small-scale biomass processing depots differs from that of large fossil fuel refineries. Like fossil refineries, the capital cost per unit of product decreases with increasing scale, a concept known as ‘economies of scale’. Unlike large refineries, a larger biomass collection area is needed for larger depots, which leads to longer transport distances and higher feedstock cost. Thus a trade-off between economies of scale and economies of transportation results in an optimal scale for biomass processing depots. Sultana et al. determined the optimal size of agricultural pellet depots to be 150,000 tonnes per year [50]. In addition to depot size, biomass moisture content affects the economics of biomass upgrading depots. Roise et al. developed a method to determine the optimum moisture content for a woody fuel production system by balancing the efficiencies of hauling and drying [51]. However, the effects of dry matter loss during on-site drying were not included in this study [51]. Sosa employed a linear programming model to optimize the moisture content of wood chips to determine the minimum delivered cost to end-users [52]. However, this was for raw biomass and not torrefied and densified solid fuels. A model that encapsulates the competing effects of economies of scale, economies of transportation, dry matter losses during storage and changing moisture content is needed to better understand the economics of torrefaction for making a renewable solid fuel.

Previous research has been conducted to estimate and compare the economics of conventional pellets and torrefied pellets [53, 54]. However, these comparisons were

performed assuming the same depot capacity and feedstock moisture content rather than on scales and moistures optimized for each type of product. A comparison of production costs for conventional and torrefied pellet systems is needed when each system is optimized for depot scale and moisture content.

In this study, depot size and biomass moisture were simultaneously optimized for the production of woody biofuels. For the first time, three technology scenarios, including conventional pellets (CP), moderately torrefied pellets (TP1), and severely torrefied pellets (TP2), were compared based on the optimum total production cost at the upgrading depot's exit gate. The effects of biomass field conditions and weather conditions were also studied to determine the behaviors of these three scenarios in different geographical regions. Costs are accrued from wood chip purchase to the upgrading depot's exit gate, while subsequent transportation and grinding at end-users are objects of future study. Minimizing the costs inherent in torrefaction energy systems is critical to be competitive with other renewable alternatives under the mandates in place in several States within the U.S.A.

3.3. Methods

3.2.1. Process description

Three different scenarios are considered for upgrading wood chips in this study, including: 1) the use biomass pellets from raw wood, referred to as conventional pellets (CP), 2) low temperature torrefaction and pelletization to upgrade biomass properties (TP1), and 3) high temperature torrefaction followed by pelletization (TP2). The scope of the three scenarios includes everything from purchasing wood chips from plantation owners through processing at the upgrading depot. The scope encompasses the process

configurations for the CP and TP scenarios as depicted in Figure 3.1 (a) and Figure 3.1 (b) respectively.

3.2.2. On-site drying and hauling wood chips

Initially, wood chips are bought in the field at a price of \$50 per dry tonne. Wood chips are dried in the field before hauling to reduce transport and drying costs. Pecenka et al. stated that 6 to 8 months of on-site drying can reduce moisture contents from 60 wt.% to 35 wt.%, depending on the weather conditions [55]. After on-site drying, wood chips are hauled to the upgrading depot by standard semi-trailers, which have cargo capacities of 25 tonne and 100 cubic meters.

3.2.3. Drying

Rotary dryers are employed to reduce the moisture content of biomass. For CP, the biomass moisture content must be reduced to an appropriate range. If the moisture content is too low (below 4%), pellets tend absorb water, elongate and become fragile in a few days. Water in biomass acts both as a natural binder and as a lubricant during pelletization, so appropriate moisture levels improve durability. In general, a moisture content range of 6% to 15% was recommended in order to produce pellets with low elongation and high durability [56-58]. For CP, biomass was assumed to be dried by rotary dryers to a moisture of 13 wt.% , equaling the equilibrium moisture in pellets if the relative humidity is 70%. For the TP scenarios, biomass was dried to a moisture of 6 wt.% to reduce the amount of heat needed for torrefaction.

supply dryer heat. As shown in Figure 3.1 (a), a portion of the dried wood chips is fed into biomass burners for the CP scenario. For the TP scenarios, the gaseous co-product of torrefaction is used as fuel to heat the torrefiers and dryers as shown in Figure 3.1 (b). Direct biomass combustion can also be employed in the TP scenarios when the heat from the gaseous co-product is insufficient. A lower heating value of 17.6 MJ/kg (dry weight basis) was used to calculate the mass of wood chips needed for combustion [59]

3.2.4. Torrefaction

For the TP scenarios, torrefaction, a biomass upgrading technology, is integrated with CP to produce torrefied pellets. As shown in Figure 3.1, torrefaction is placed between drying and grinding to reduce the needed grinding energy and thus save cost. A moving bed torrefaction reactor was selected in this study because of low maintenance and capital costs. The mass and energy yields for the TP scenarios in Table 3.1 were obtained from previous literature [59].

3.2.5. Grinding

Grinding in a hammermill is performed between pelletization and drying. An appropriate particle size is important as it significantly impacts energy consumption and the physical properties of the pellets. The grinding energy requirement grows exponentially with decreasing biomass particle size. Larger particle sizes lead to smaller comminution energy requirements, but the lower density and durability of the pellets is undesired. Pellets are prone to preset crack when particle size exceeds 1 mm. A particle size of 0.6 to 0.8 mm is usually recommended to produce high quality pellets [60, 61]. The milling screen in the hammer mill controls the particle size after comminution. In this study, a hammermill screen size of 4.6 mm, which leads to an average particle size of

0.8 mm $\pm$ 0.41, was selected to achieve desirable pellet properties. A grinding energy of 400 kJ per kg of dry willow chips was assumed for the CP scenario to achieve this particle size [62]. The savings in grinding energy for TP1 and TP2 were determined to be 60% and 90% respectively [63].

Table 3.1 TP scenario process and product assumptions [59]

Parameters	TP1	TP2
Reaction temperature (°C)	250	300
Residence time (min)	30	10
Mass yield of solid product (wt.% of dry biomass)	87%	67%
Energy yield of solid product (energy % of biomass LHV)	97%	80%
Heat demand during torrefaction (kJ/kg of dry biomass)	87	124

3.2.6. Pelletization

The equipment involved in pelletization includes pellet mills, coolers and screeners. A ring die pellet mill, widely used in pelletization, was adopted in this study. For those pellet mills with large throughput, cooling of the pellets is necessary to reduce fire risk. Counterflow coolers then follow the pellet mills to reduce the temperature to ambient conditions. Unshaped pellets and biomass fines generated during cooling are screened separated and recycled to the mills. Properly shaped pellets are collected and stored in pellet storage facilities. In this study, binders are not added in CP because lignin acts as a natural binder during pelletization in lignin-rich woody biomass [8, 64, 65]. Binders may or may not be required when using torrefaction as structural modifications to the lignin increase its tack point temperature, making it difficult to pelletize torrefied wood. To overcome pelletization difficulties in the TP scenarios, starch is added as a binder to a level of 3 wt.% to reduce particle abrasion, dust formation and moisture penetration.

3.2.7. Storage

Wood chips have unstable and heterogeneous moisture contents when uncovered outdoors owing to variable weather conditions. Therefore, storage lots with roofs are needed at upgrading depots to ensure continuous supply of feedstock that has a stable moisture content. Storage capacity was fixed to supply two weeks of feedstock [64]. Torrefied biomass is also hydrophobic and biologically recalcitrant, so torrefied pellets in this system are stored outdoors, whereas conventional pellets are stored in silos. The equilibrium moisture contents of CP, TP1 and TP2 were assumed to be 13%, 8%, and 7%, respectively, with a relative humidity of 70% [66].

3.2.8. Economic analysis

Table 3.2 lists unit capital investments, unit sizes, scale factors, maximum possible sizes, maintenance costs, power required, and utilization periods of main equipment in the conversion depot. All the capital investments were inflated to 2014 USD using the chemical engineering plant index. The straight-line method was adopted in this study to estimate depreciation cost. Labor costs at the depot were scaled as a power function using an exponent of 0.25, as described by Peters et al. and Leboireiro et al. [67, 68]. Electricity was assumed available at 7.32 cents/kWh, which is the U.S. average industrial price in 2014. The depot on-line time was set at 90%, meaning that 10% of the time is used for maintenance and repairs.

Capital investment is commonly scaled using a power function based on a predetermined scale factor. Each equipment item was scaled to its maximum commercial size using a power function, employing multiples of equipment in parallel when flow rates exceed maximum capacity. Equation (1) was used to calculate the capital

investment for each equipment item.

$$CI = (N - 1)CI_{max} + CI_{base} \left(\frac{S}{S - (N - 1)S_{max}} \right)^{sf} \quad (1)$$

Where CI is the capital investment, CI_{base} is the capital investment of the base unit size, CI_{max} is the capital investment of the maximum size, S represents the equipment size, S_{max} is the maximum size, sf is the scale factor, and N is the total required number of equipment items.

Table 3.2 Equipment specifications for upgrading depots.

Equipment	CI_{base}^a	Unit size	Scale factor	Max size	Maintenance cost ^b	Electricity usage (kwh/t)	Expected life (years)
Feeder	17,367	1dt/h ^c	0.57	6dt/h	3%	5	15
Rotary drum dryer	820,194	1t _{water} /h ^d	0.6	6t _{water} /h	3%	26	15
Hammer mill	55,404	1dt/h	0.6	13dt/h	15%	50	10
Pellet mill	84,805	1dt/h	0.85	6dt/h	18%	100	10
Cooler	27,713	1dt/h	0.58	30dt/h	3%	4	15
Screen shaker	8,756	1dt/h	0.6	13dt/h	3%	4	10
Solid fuel burner	95,483	1 MW	0.7	408MW	3%	5	10
Torrefaction system ^e	673,283	1dt/h	0.6	3.8dt/h	3%	10	15
Conveyor	32,409	1dt/h	0.75	14dt/h	3%	4	10
Loader/lifter	24,372	1dt/h	-	-	3%	-	10
Pellets storage silo	490	1dt	0.85	5400dt	1.5%	-	20
Wood chips storage	89	1dt	0.85	-	1%	-	20

^a: CI_{base} is the capital investment at the unit size.

^b: Annual maintenance cost is based on the percent of the capital investment of equipment.

^c: dt/h represents dry tonne of product per hour

^d: t_{water}/h stands for tonne of evaporated water per hour

^e: Torrefaction system includes moving bed reactors, gas burners, gas blowers and heat exchangers;

Reference: [8, 9, 12, 14, 34, 64, 69]

3.2.9. Hauling distance

The willow plantations were assumed to be uniformly distributed. Hauling

distance was calculated by equation (2) [70].

$$d_{hauling} = (2\tau / 3)\sqrt{P \times \pi / M} \quad (2)$$

Where, $d_{hauling}$ is the hauling distance, P denotes the annual biomass needed for the conversion depot, τ is the road winding factor (assumed to be 1.8—a common value in Michigan), and M represents the biomass availability. Willow plantations are to be established within existing timberland. Assuming Michigan conditions, 52% of the harvest area was assumed to be timberland that is capable of delivering 0.3 dry tonnes of willow chips per hectare [71]. Harvestable yield would be increased if additional feedstocks are considered, though only willow is presented in this analysis.

The values of τ and M can vary significantly between different regions. To capture the effects of this variability, a dimensionless group ‘F’ is related to τ and M by equation (3). F represents the accessibility and dispersion of biomass that is available to produce solid fuel. This dimensionless number was changed by $\pm 50\%$ to investigate the effects of biomass field conditions.

$$F = (1 / \tau)\sqrt{M/M'} \quad (3)$$

Where, M' is unit biomass availability (1 dry tonne/(km²*year))

Equation (4) is derived by substituting equation (3) into equation (2). Therefore, biomass hauling distance in equation (4) is a function of P , which is determined by the depot size and F .

$$d_{hauling}(F, P) = (2 / 3F)\sqrt{P\pi / M'} \quad (4)$$

3.2.10. On-site drying cost

Dry matter loss occurs during on-site drying due to biological degradation. As per

Garstang et al. [72], a dry matter loss of 1 wt.% per month is assumed to predict mass loss during field storage of willow. This assumption is adequate for the first year of drying, but less accurate in successive years. When the drying time is longer than 12 months, the rate of dry matter loss decreases exponentially and approaches zero. In this study, the dry matter loss was assumed to be a linear function of the drying time and on-site drying longer than 12 months was not considered in this study. Besides dry matter lost, on-site drying increases the interest cost because feedstock usage is delayed. Wood chips are purchased before on-site drying but not used until the desired moisture is reached. Therefore, the biomass cost at the upgrading depot gate can be calculated using equation (5).

$$BC_{gate}(t_{days}) = \frac{(1+r)^{t_{days}} * BC_{purchased}}{(1 - t_{days} / 3000)} \quad (5)$$

Where BC_{gate} is the biomass cost at the conversion depot gate, t_{days} is the on-site drying time required in days, $BC_{purchased}$ is the biomass purchased cost in the field before on-site drying, and r is the daily interest rate [51].

The time required to reach a certain moisture after on-site drying is a function of the final moisture content, temperature, relative humidity and precipitation. Due to annual weather variations, drying duration is a function of the calendar month. Equation (6) was derived from the model of Roise et al. and used to estimate the monthly required drying time in this study [51].

$$t_{days, i}(MC) = \frac{(MC_0 - MC)}{0.81 * (MC_0 - MC_{eq}) * \exp(0.019 * Temp_i - 0.099 * Hum_i - 0.115 * Precip_i)} \quad (6)$$

Where ‘i’ is the i^{th} month when biomass is hauled to the conversion depot ($i=1$ to 12), MC is the final biomass moisture content after on-site drying, MC_0 is the initial biomass moisture (assumed to be 60 wt.%), and $MCEq$ is the equilibrium moisture (assumed to be 4.75 wt.%). $Temp_i$, Hum_i and $Precip_i$ represent the average temperature, relative humidity and precipitation in the entire on-site drying period, respectively. Michigan monthly weather data for 2014 were adopted in this study.

Biomass cost for the i^{th} month was calculated by substituting equation (6) into equation (5). The average biomass cost as shown in equation (7) was used to calculate the total production cost. Biomass cost is mainly determined by the biomass purchased cost before on-site drying and biomass moisture after on-site drying.

$$BC_{gate}(MC) = BC_{gate}(t_{days}) = average[BC_{gate,i}(t_{days,i})] \quad (7)$$

3.2.11. Optimization of depot size and biomass moisture content

The total production cost (TPC) including the variable cost (VC), fixed cost (FC) and biomass hauling cost (HC) was estimated as a function of depot size and biomass moisture. Equation (8) was used to calculate the total production cost. VC includes the on-site drying cost and is thus dependent on the biomass moisture content. FC is a function of depot size and is thus subject to economies of scale. HC is dependent on the depot size, F, and biomass moisture. For the base case, F was fixed at a value of 10 which represents the field conditions for willow in Michigan. MATLAB software was used to perform the numerical calculation in this study. 2.5×10^5 values of TPC were calculated by using 500 values of biomass moisture and 500 values of depot size. The minimum TPC was selected and the optimum values of biomass moisture and depot size were

determined.

$$TPC = VC(MC) + FC(size) + HC(size, F, MC) \quad (8)$$

3.4. Results

3.3.1. Optimized parameters

The total production costs of each scenario are determined and compared to determine the efficacy of torrefaction for upgrading biomass. First, depot capacity and biomass feedstock moisture capacity were optimized together to determine the minimum total production cost. Optimal depot capacity includes the competing effects of economies of scale and economies of transportation, while optimal moisture affects depot capacity through transportation cost. Figure 3.2 (a) shows total production cost as a function of depot capacity at the optimal moisture content for each scenario. For all three scenarios, the production costs steeply increase when the capacities are below 60 MW, so small depots are not as economical. CP has the highest optimal capacity of 92MW, while the optimal capacities of TP1 and TP2 are reached at 84 MW and 82 MW, respectively. High biomass moisture content, equating to high hauling cost, also influences the optimal capacity and hence total production costs. As shown in Figure 3.2 (a), CP and TP1 have very similar optimal biomass moisture contents and therefore have almost parallel total production cost functions. Conversely, TP2 is more affected by capacity than TP1 beyond capacities of 80 MW because of the increased cost of hauling biomass with higher moisture content. Although there is no significant difference between TP1 and TP2, note that it is slightly more desirable to build facilities operating at low torrefaction temperatures.

Figure 3.2 (b) shows the total production cost as a function of biomass moisture content after on-site drying at the optimal capacity for each scenario. It is not economical when biomass is dried to lower than the optimal moisture content when considering mass loss and interest cost during on-site drying. The problems with high moisture content feedstocks are higher hauling costs and higher drying cost. According to the results, CP has the lowest optimal moisture content of 32%. For CP, direct biomass combustion provides the drying heat, so low moisture content is needed to reduce feedstock costs. Conversely, the torrefaction scenarios produce heat by burning the gaseous co-product and thus reduce or even avoid direct biomass combustion. For TP1 only 13 wt.% of the biomass becomes combustible gas, enough to heat the torrefier, but is insufficient for also drying the biomass. In TP1, an additional 10 wt.% of biomass must be directly combusted to provide the needed drying energy. Thus TP1 has a slightly higher optimal biomass moisture content than CP but much less than TP2, which produced sufficient gas for drying and torrefying biomass. For TP2, 20% of the energy in biomass is retained in the torrefaction gas. By supplying this gaseous energy to the dryer, no biomass is needed for direct combustion to make heat. Thus, TP2 allows a high optimal biomass moisture content and can be economical even if biomass moisture is high. However, the total production cost of TP2 steeply increases when the biomass moisture goes below 40 wt.%, as it is assumed that the excess energy from combustible gas is wasted. It is therefore crucial to operate high torrefaction temperature processes at the optimal biomass moisture, or have a separate use for this extra thermal energy.

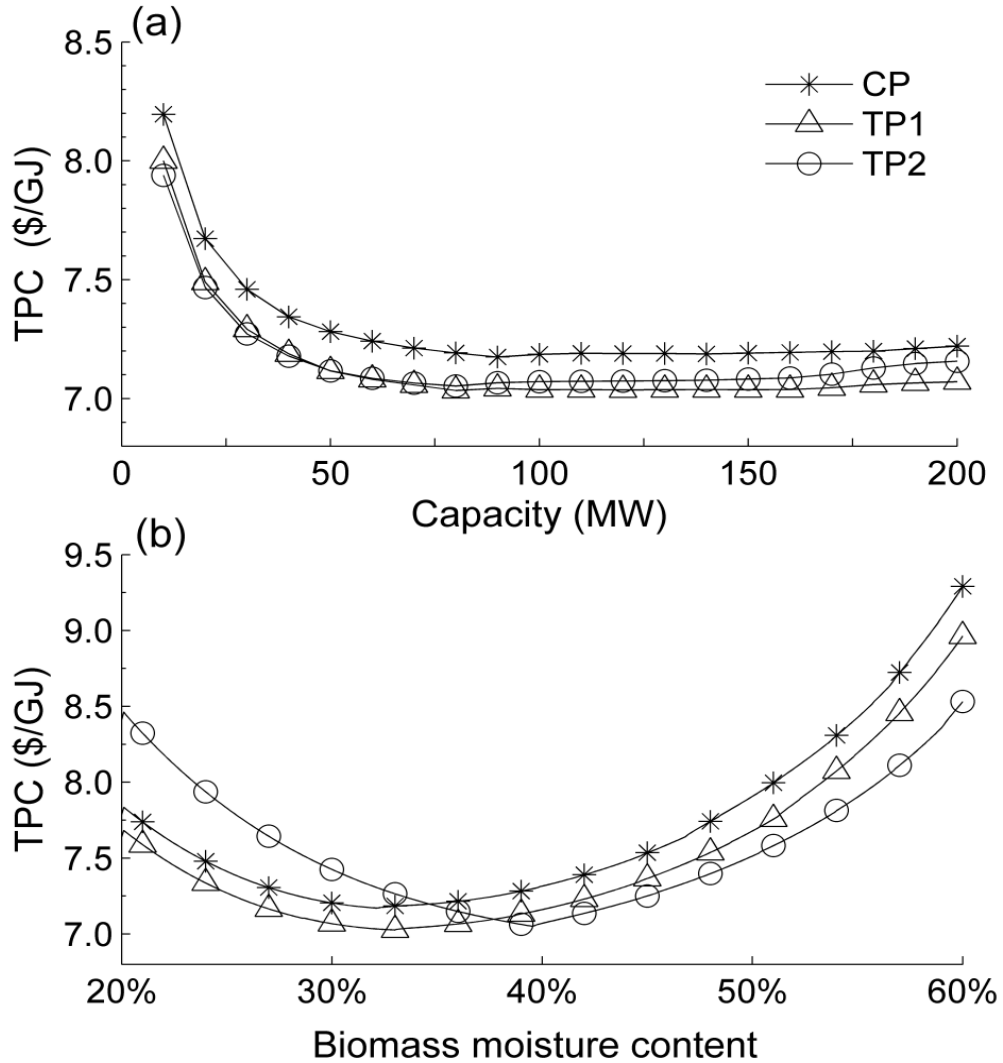


Figure 3.2. (a) Minimum total production cost vs. capacity at the optimal biomass moisture content for three scenarios (optimal moisture content: 32%, 33% and 40% for CP, TP1 and TP2, respectively). (b) Minimum total production cost vs. biomass moisture content after on-site drying at the optimal capacity for three scenarios (optimal capacity: 92MW, 84MW and 82MW for CP, TP1 and TP2, respectively). Total production cost and capacity are based on the lower heating content in the final product with units of \$/GJ and Megawatt. Biomass moisture content after on-site drying is the wt% of wet biomass.

When considering moisture, the range of low cost operation is greater for TP1 and TP2 than for CP, with TP1 having the greatest range as seen in Figure 3.2 (b). This can be observed in the contour map shown in Figure 3.3 (b) and (c), where CP and TP2 have

much narrower operating ranges of biomass moisture for less than \$7.2 per GJ. Considering the uncertainty of on-site drying conditions such as weather, in this respect, TP1 is more desirable because of a tendency for lower cost and a lower sensitivity to biomass moisture than TP2.

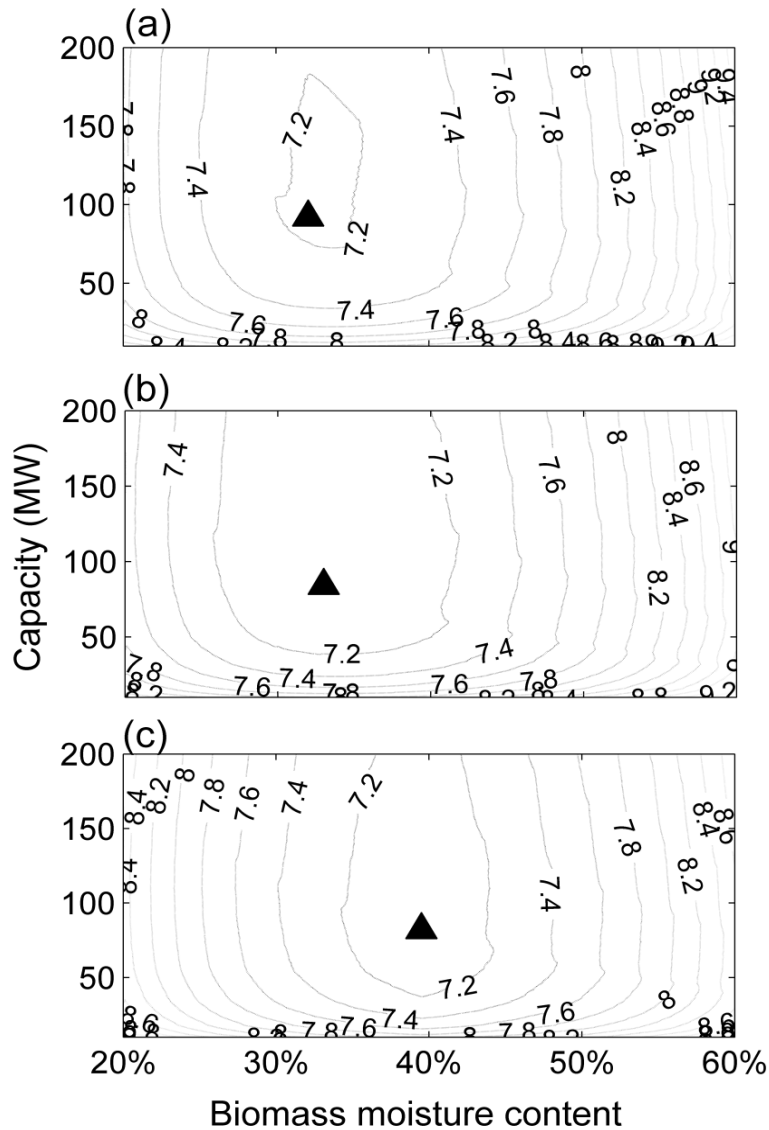


Figure 3.3. Total production cost contour plots with capacity and biomass moisture content for a) CP, b) TP1, and c) TP2. Total production cost and capacity are based on the lower heating content in the final product with units of \$/GJ and Megawatt, respectively. Biomass moisture content after on-site drying is the wt% of wet biomass.

Overall, the minimum total production cost for each scenario in Table 3.3 was

determined using optimized values of biomass moisture content and depot capacity. Torrefied pellet scenarios (TP1 and TP2) have lower total production costs than the conventional pellet scenario (CP). Torrefaction scenarios advantageously reduce the total production cost when compared to CP because its product has a lower equilibrium moisture content and a higher LHV. TP2 has slightly higher production cost than TP1 because of mass loss during more severe torrefaction. TP2 has a noticeably higher optimal biomass moisture content than TP1 and CP, owing to the increased amount of combustible gas that is available for vaporizing water. Both TP depots have optimum capacities that are lower than the CP depot because TP depots need more extensive drying as torrefaction requires low feedstock moisture contents.

Table 3.3 Optimized parameters for three scenarios: CP, TP1 and TP2.

	CP	TP1	TP2
Minimum total production cost (\$/GJ _{LHV})	7.17	7.03	7.05
Optimum biomass moisture content (wt.%)	32%	33%	40%
Optimum depot capacity (MW _{LHV})	92	84	82

Note: Optimum biomass moisture content is the moisture of feedstock after on-site drying and before entering the conversion depot. Conversion cost at the depot is all the other cost except hauling cost and feedstock cost, including costs of depreciation, maintenance, labor, electricity and etc

3.3.2. Costs distributions for optimized scenarios

Figure 3.4 shows the cost distributions at the optimized conditions for three scenarios. For all three scenarios, biomass costs contribute the most to the total production costs. Thus, reducing the biomass cost is crucial to lower the total production cost. Biomass costs include the field price of biomass, costs due to mass loss during on-site drying, and interest costs incurred during on-site drying. TP1 consumes about 10 wt.% more biomass than CP as the torrefied biomass yield is negatively affected by both mass loss and direct combustion needed for drying. However, TP1 still has a slightly lower

biomass cost than CP and TP2 because of the higher LHV in the torrefied pellets. When the torrefaction temperature is too high, mass loss during torrefaction may increase the biomass costs despite high LHV in torrefied pellets. Compared to TP1, TP2 has a higher LHV by 10%, but 2.4 times the mass loss during torrefaction, which results in a slightly higher biomass cost.

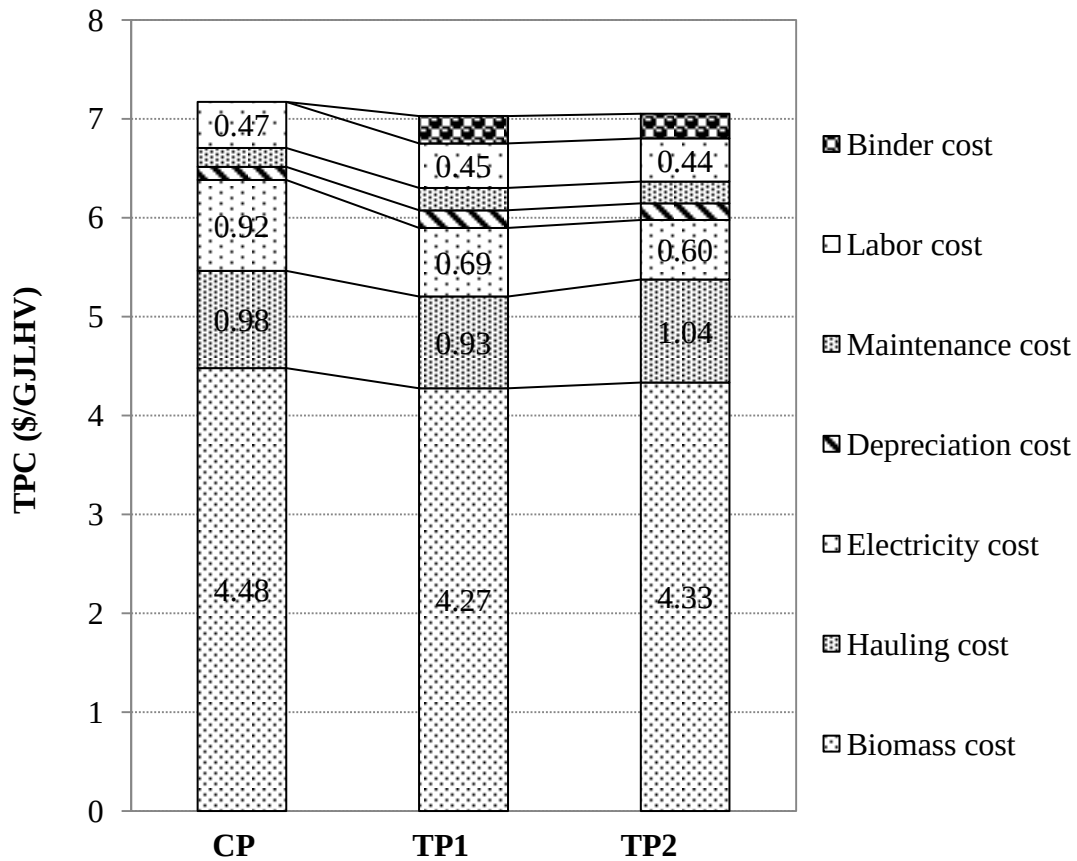


Figure 3.4. Costs distributions at the optimized conditions for CP, TP1, and TP2.

As shown in Figure 3.4, hauling raw biomass to the depots contributes the second largest cost. Of the costs considered, TP1 has lower hauling costs than CP or TP2. CP requires more biomass to produce 92 MW of energy than TP1 requires to make 84 MW of energy, owing in part to the lower LHV of CP products. TP2 hauling costs are higher than TP1 because its higher moisture content results in transporting more water.

Electricity cost, the third highest cost, is mostly a function of grinding and pelletization. Grinding costs can be reduced by increasing torrefaction severity, thus making the torrefied wood product more friable. For this reason, the electricity cost for TP2 is the lowest. TP1 and TP2 have higher depreciation costs because of the torrefier capital investment. TP2 has a higher depreciation cost than TP1 because the high optimal moisture content raises the capital cost of the dryer. Labor costs are slightly lower for the torrefaction scenarios because of the high LHV of the product. Binder costs were assumed necessary for the torrefaction scenarios but not CP. Torrefaction modifies the structure of lignin, which is a natural binder during pelletization. After torrefaction, lignin's increased tack point temperature makes torrefied wood hard to pelletize and therefore extra binders are assumed necessary to make durable torrefied pellets.

3.3.3. Weather conditions

On-site drying behavior depends on weather conditions such as temperature, relative humidity and precipitation. These weather condition parameters were changed by $\pm 10\%$, as shown in Figure 3.5, to study the effects of weather on the optimal total production cost, biomass moisture and capacity. A change of -10% represents a humid and cold region where a long drying period is required, while $+10\%$ refers to a dry and warm region where on-site drying is easy to perform.

As shown in Figure 3.5 (a), CP and TP1 are both linearly affected by the weather conditions and similarly parallel to each other. This illustrates that the limited mass loss during torrefaction does not greatly influence the sensitivity of TP1 to weather conditions when compared with CP. TP1 always has a lower optimal total production cost than CP because the higher LHV product of TP1 leads to lower feedstock requirements. TP2 has

the same total production cost as TP1 near the base weather conditions. In humid and cold regions, TP2 has the lowest cost among the three scenarios because of the greater amount of combustible gas allows for a higher moisture content. This illustrates that high torrefaction temperature is suitable to be applied in humid regions where woody biomass is difficult to field dry. However, TP2 becomes the most cost-intensive scenario in dry and warm regions. When woody biomass can be dried to a low moisture with a short period in field, CP and TP1 are more cost effective than TP2 because of lower mass loss. As expected, the monotonically decreasing functions for the three scenarios in Figure 3.5 (a) show that producing either conventional pellets or torrefied pellets in the dry and warm regions is more economical than in the humid and cold regions.

Figure 3.5 (b) shows the effects of weather conditions on the optimal biomass moisture content. All three scenarios result in decreasing functions as weather conditions trend from humid to dry. Moisture contents of CP and TP1 are almost the same in all regions as the energy available in the torrefaction gas of TP1 is limited. TP2 has more available energy in torrefaction gas, so high moisture contents can be capably managed. However, TP2 costs more when conditions are dry, again owing to increased mass loss.

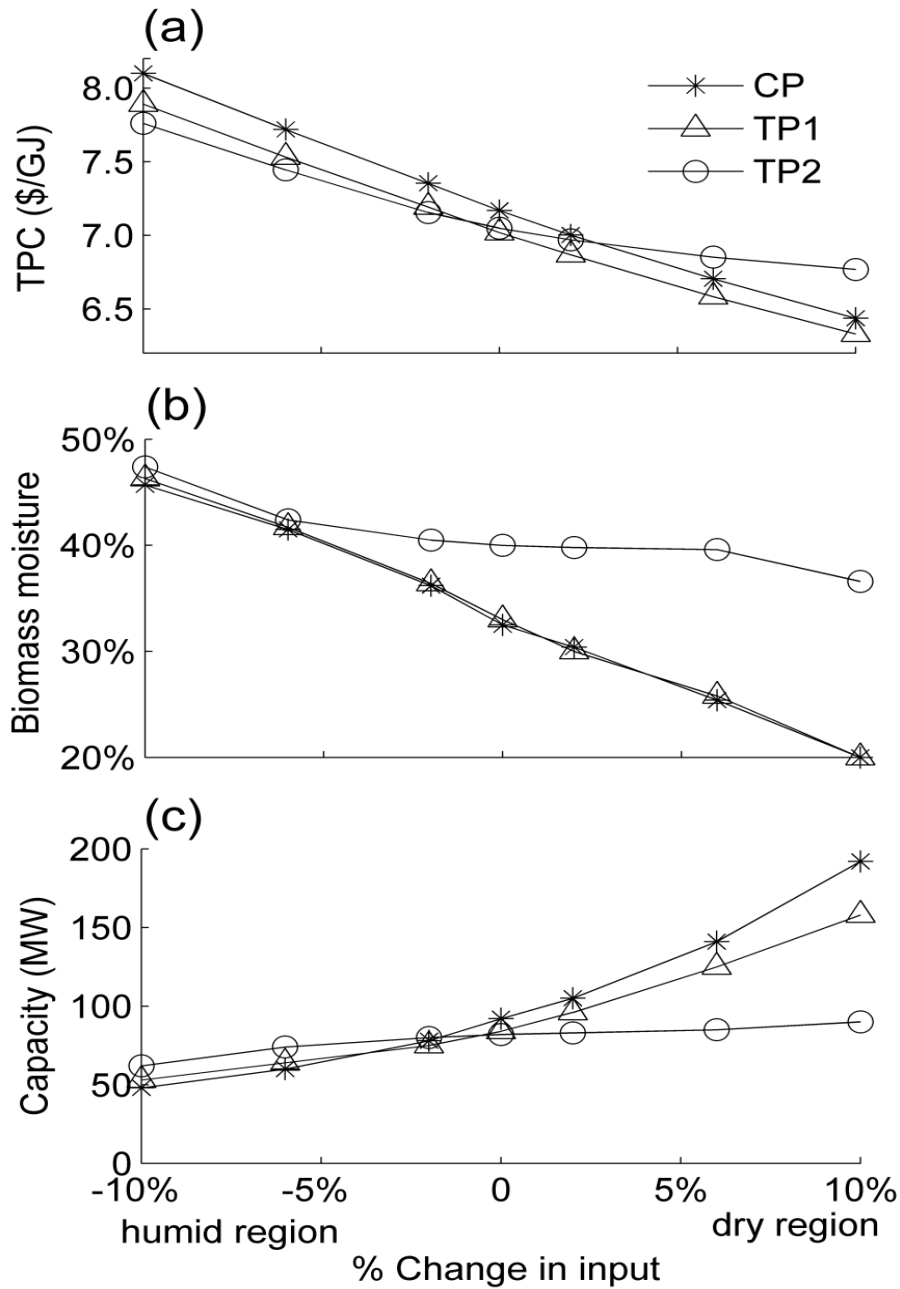


Figure 3.5. Effects of weather conditions on the optimized parameters: a) minimum total production cost; b) optimal biomass moisture content; and c) optimal depot size. Total production cost and capacity are based on the lower heating content in the final product with units of \$/GJ and Megawatt, respectively. Biomass moisture content after on-site drying is the wt% of wet biomass.

Figure 3.5 (c) shows the effect of weather conditions on the optimal depot

capacity. In dry regions, large depot capacities are required for CP and TP1 because the low optimal biomass moisture content reduces biomass hauling cost. Conversely, For TP2, the optimal capacity does not vary much according to weather conditions because the optimal biomass moisture is relatively flat as in Figure 3.4b. CP is the most sensitive to weather conditions among the three scenarios as it requires more biomass for direct combustion to supply dryer heat. As more biomass is collected from ever larger distances, the biomass hauling cost increases. Further, long hauling distances increase the sensitivity of hauling cost to moisture content. For this reason, larger CP facilities can be built in dry regions than in humid regions.

3.3.4. Effects of field conditions - F

Biomass field conditions, as specified by the road winding factor and biomass availability, vary in different regions. The biomass field condition dimensionless group, F , was varied from 5 to 15 to study the effects of field conditions, on the three scenarios. A large F equates to a low road winding factor or high biomass availability; a condition where biomass can be hauled to depots at low costs. A small F refers to a combination of a very tortuous road or extremely diffuse biomass, a situation that is cost intensive. Three scenarios are compared based on the minimum total production cost, optimal biomass moisture and optimal depot capacity under different values of F in Figure 3.6.

As shown in Figure 3.6 (a), the production costs of all three scenarios are decreasing functions of F because of the hauling cost reduction at the large F . This illustrates that the large F region is more suitable than the small F region to build CP or TP depots based on economic criteria. It also can be observed in Figure 3.6 (a) that F has no impact on the cost differences of the three scenarios. TP1 always has the lowest cost

among three scenarios in both the small F region and the large F region, a result explained by the low amount of feedstock needed and high torrefaction mass yield.

Figure 3.6 (b) shows the effect of F on the optimal moisture content for each scenario. TP2 is not affected by F because the optimal moisture of 40 wt.% is dominated by the large amount of energy in the gaseous co-product and not by the field conditions. CP and TP1 are affected by the field conditions and increasing F as hauling more water becomes cost effective in regions where biomass is concentrated and roads are less tortuous. Figure 3.6 (c) shows the effect of F on the optimal depot capacity for each scenario. All three scenarios are linearly affected by F and allow for large capacities at higher values of F because of the reduction in hauling cost. Optimal CP depots are always larger because TP depots need to vaporize more water prior to torrefaction, a fact that leads to expensive dryers. Although TP2 biomass has much higher moisture than TP1, TP scenarios have similar optimal capacities at all F values. The reason that TP1 and TP2 have similar costs is that the higher hauling costs in TP2, due to more moisture, is counterbalanced by the higher LHV of its products, leading to lower feedstock costs on a dry basis.

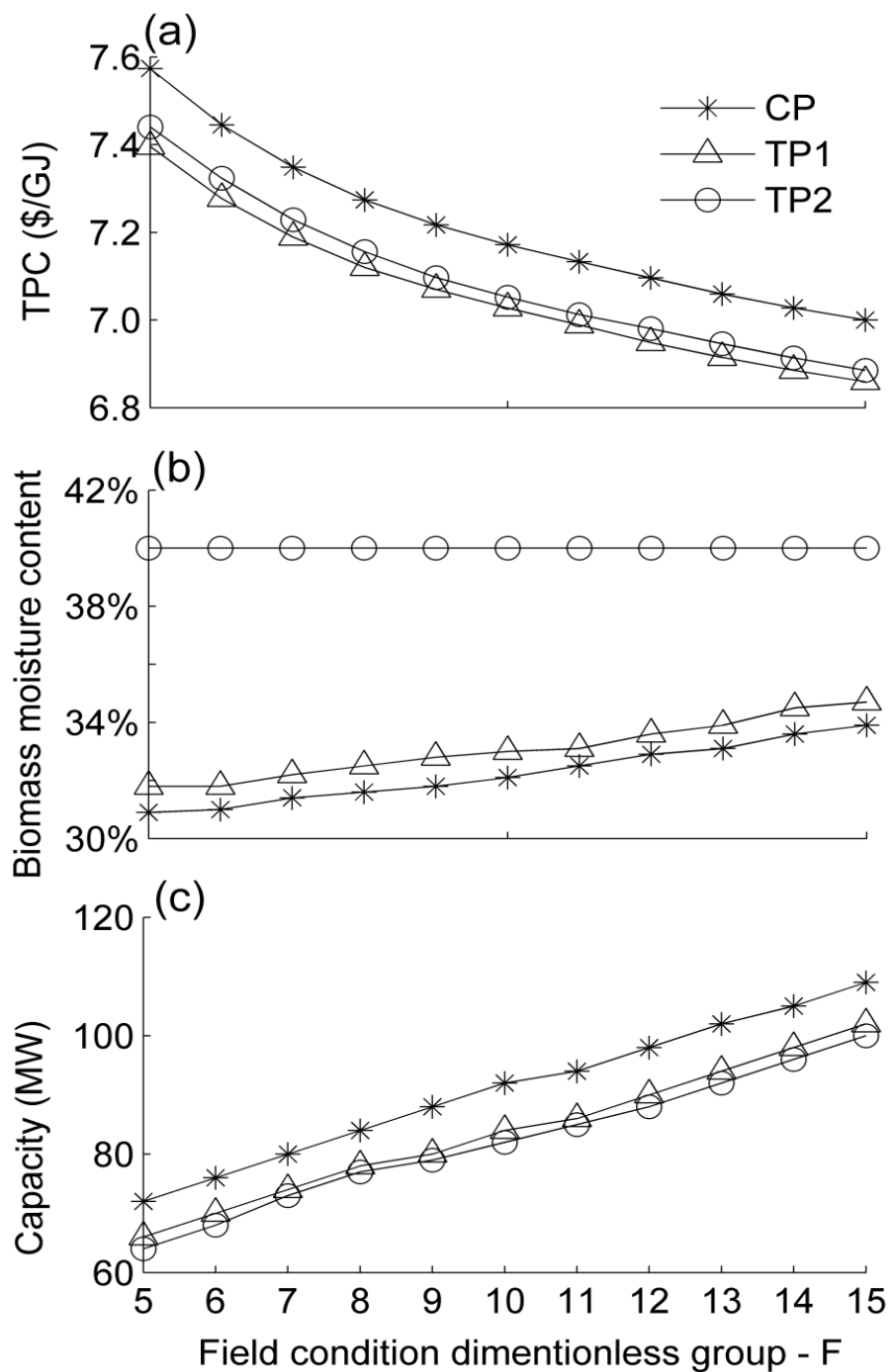


Figure 3.6. Effects of F on the optimized parameters: a) minimum total production cost; b) optimal biomass feedstock moisture content; c) optimal depot capacity. Total production cost and capacity are based on the lower heating content in the final product with units of \$/GJ and Megawatt, respectively. Biomass moisture content after on-site drying is the wt% of wet biomass.

3.3.5. Effects of biomass purchased cost

The cost of purchasing wood chips at field before on-site drying varies in different regions. Biomass purchased cost was varied from \$25/dry tonne to \$75/dry tonne to study the effects on the optimal total production costs of three scenarios. As shown in Figure 3.7, with the decreasing biomass purchased cost, the total production cost decreases linearly. For all three scenarios, the total production cost is very sensitive to biomass purchased cost. When the wood chips are purchased at a cost of \$25/dry tonne at field, the total production costs of three scenarios are below \$5/GJ.

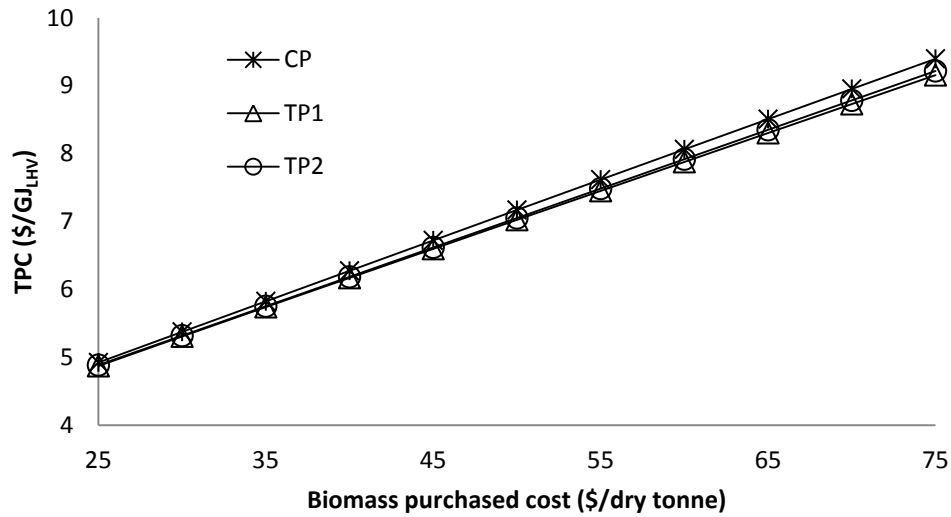


Figure 3.7 Effects of biomass purchased cost at field on the optimal total production costs

3.5. Conclusions

The optimal depot sizes and biomass moisture contents after on-site drying were determined to obtain the minimum total production costs for three comparable scenarios: conventional pellets (CP), light torrefied pellets (TP1) and heavy torrefied pellets (TP2). Biofuel from TP1 has a higher LHV than biofuel from CP and a higher torrefaction yield than TP2, resulting in the lowest optimal production cost at the upgrading depot exit gate.

Effects of biomass field conditions show that a high F (concentrated biomass distribution and small road winding factor) results in a low optimal production cost for all three scenarios. Changing the weather conditions reveals that it is more economical to build a conversion depot in dry regions than in humid regions. In humid regions, TP2 becomes more economical because of the energy obtained from combusting the gaseous co-product of torrefaction. In conclusion, application of TP2 is justified in humid regions, while adopting TP1 is less costly in dry regions.

3.6. Acknowledgements

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Chapter 4 Techno-economic Analysis of Green Aromatics Production from Renewable Biomass

Li Chai, Christopher M. Saffron

4.1. Abstract

A process of converting renewable biomass into green aromatics was investigated. Economic analysis shows a total fixed capital investment equal to \$214 million was found necessary to purchase and install the necessary equipment to process 2,000 tonnes of biomass every day. Variable and fixed operating costs were estimated to be \$1.22 and \$1.85 per gallon of BTEX, respectively. Biomass and catalyst respectively contributes 20% and 17% to the total production costs.

Keywords: catalysis; pyrolysis; BTEX; biomass

4.2. Introduction

Green aromatics, such as benzene, toluene, ethyl benzene and xylenes (BTEX), are intermediates for the synthesis of terephthalic acid. When co-polymerized with ethylene glycol from bio-ethanol, green polyethylene terephthalate (PET) can be used to manufacture containers for beverage industry. The process, consisting of pyrolysis and catalysis, will transform renewable feedstocks and waste streams into value-added BTEX products[73, 74]. Pyrolysis, heating without oxygen, is an inherently flexible approach to fragment a wide array of biomass varieties into a mixture of smaller molecules.

Positive socio-economic benefits include domestic and international jobs creation, capital retention and investment in rural communities, increased profitability and reduced carbon dioxide emissions resulting from waste conversion into BTEX. In addition to reduced emissions upon PET manufacture, significant carbon reductions are anticipated upon deployment of this process as the solid bio-char co-product can be land applied to

sequester carbon. As the carbon in bio-char mineralizes to carbon dioxide at very slow rates, this process can become “carbon negative” when bio-char is returned to agricultural or silvicultural systems as a nutrient amendment. Also, the carbon credits acquired in a cap and trade system for sequestering carbon as bio-char can further enhance the economic viability of this process.

The goal of this study is to conduct economic analysis for a process that is locally deployable for producing BTEX from plant biomass. A process for converting plant biomass to mono-aromatics was devised to supply intermediates for alkylation and isomerization to p-xylene for co-polymerization with ethylene glycol to make polyethylene terephthalate (PET). Pyrolysis and catalysis are the core transformation technologies used for biomass to mono-aromatics. Benzene, toluene, ethylbenzene and xylenes (esp. p-xylene) are the desired products of this approach, hereto referred to as BTEX. Figure 4.1 depicts the process flow diagram with the arrangement of equipment to produce a BTEX-rich intermediate for eventual reaction to p-xylene.

4.3. Equipment design

4.2.1. Drying

Feedstock drying is very important for thermochemical processes. Moisture present in the feed consumes process heat and results in lower process yields. Typically, a moisture content of less than 8 wt.% is recommended for the pyrolysis process. As the moisture content of biomass feedstock in this study is assumed to be 20 wt.%, a rotary dryer is employed to reduce the moisture content to 5 wt.%. The rotary dryer directly dries biomass by using heated air or process gas. Combustion gases produced from the flue gas co-product of the catalyst reactor can be used as a heat source by the rotary dryer.

An advantage of the rotary dryer is that it is less sensitive to particle size, as opposed to steam dryers which require small particle size. Rotary dryers also cost less than steam dryers, on average. It should be noted, one disadvantage of rotary dryers is the potential fire hazard due to the nature of their operation.

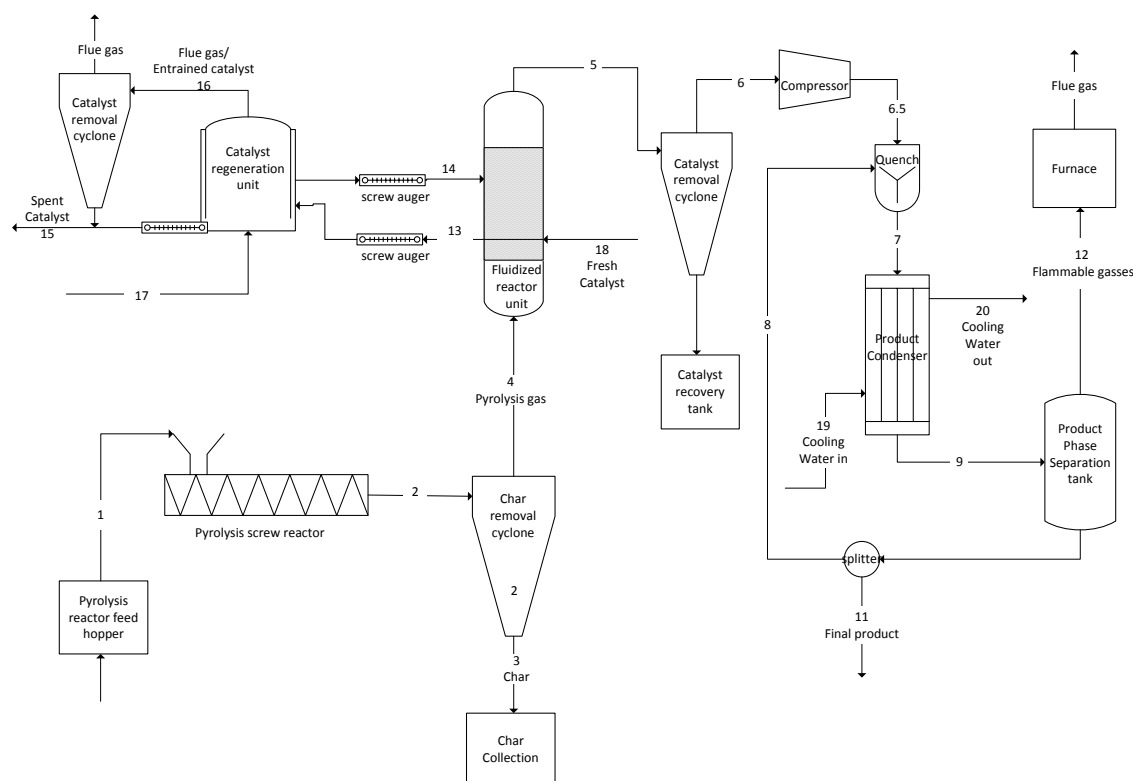


Figure 4.1 Process flow diagram for biomass conversion to BTEX. Pyrolysis, catalysis and regeneration are the major equipment items in terms of cost.

4.2.2. Pyrolysis

Pyrolysis is used to depolymerize plant biomass to create reaction products that are amenable for catalytic conversion into BTEX. In this proposed process, a screw conveyor pyrolysis reactor was selected as opposed to a fluidized-bed reactor. The screw-conveyor or extruder configuration does not require sand as a heat transfer medium to achieve high heat transfer rates. An advantage of this approach is that the non-

condensed gas is not diluted by fluidizing gas, and thus remains combustible to provide process heat. For spent coffee grounds (SCG), a temperature of 505 °C is achieved within the reactor to perform pyrolysis, which is at the optimized reaction temperature according to a series of pilot trials at MSU. The reactor is designed to contain a modest reaction pressure of 1 atm, a design constraint used to limit capital investment and reduce the need for safety shielding. Pyrolysis reactors were sized to support a total inlet flow rate of 2,000 tonnes of biomass per day, a capacity that requires ten reactors operating in parallel. The MSU pyrolysis reactor can process biomass at a rate of around 5.8 kg per hour. Mass and energy balances, shown in Figure 4.2, were based on a series of experimental trials using SCG. From the energy balance information collected from the pilot-scale screw conveyor reactor, 2.64 kW is needed to convey biomass through the reactor at the optimized reaction conditions. This energy balance data is used to calculate the electricity consumption of a reactor with a capacity of 200 tonnes per day. Heat required during the pyrolysis is provided by combustion of non-condensable gas and a portion of the bio-char co-product. An equipment cost of \$16,250 (in 2011 USD) is needed to build a lab-scale reactor according to a quote from Moulder Services Inc., a vendor of extrusion equipment. The six-tenths rule is used to scale up the screw reactor to a capacity of 200 tonnes per day, resulting in an equipment cost of \$1.27 million for such capacity. It is important to note, that pyrolysis can be performed in alternative reactor configurations, e.g. ablative, auger-type, fluidized-bed, recirculating fluidized-bed, etc., in the event that scale-up in the screw-conveyor described here is limited by heat transfer. Though many of these alternative reactors will require additional processing equipment to ensure heat transfer, it is unlikely that pyrolysis costs will dominate the total process costs.

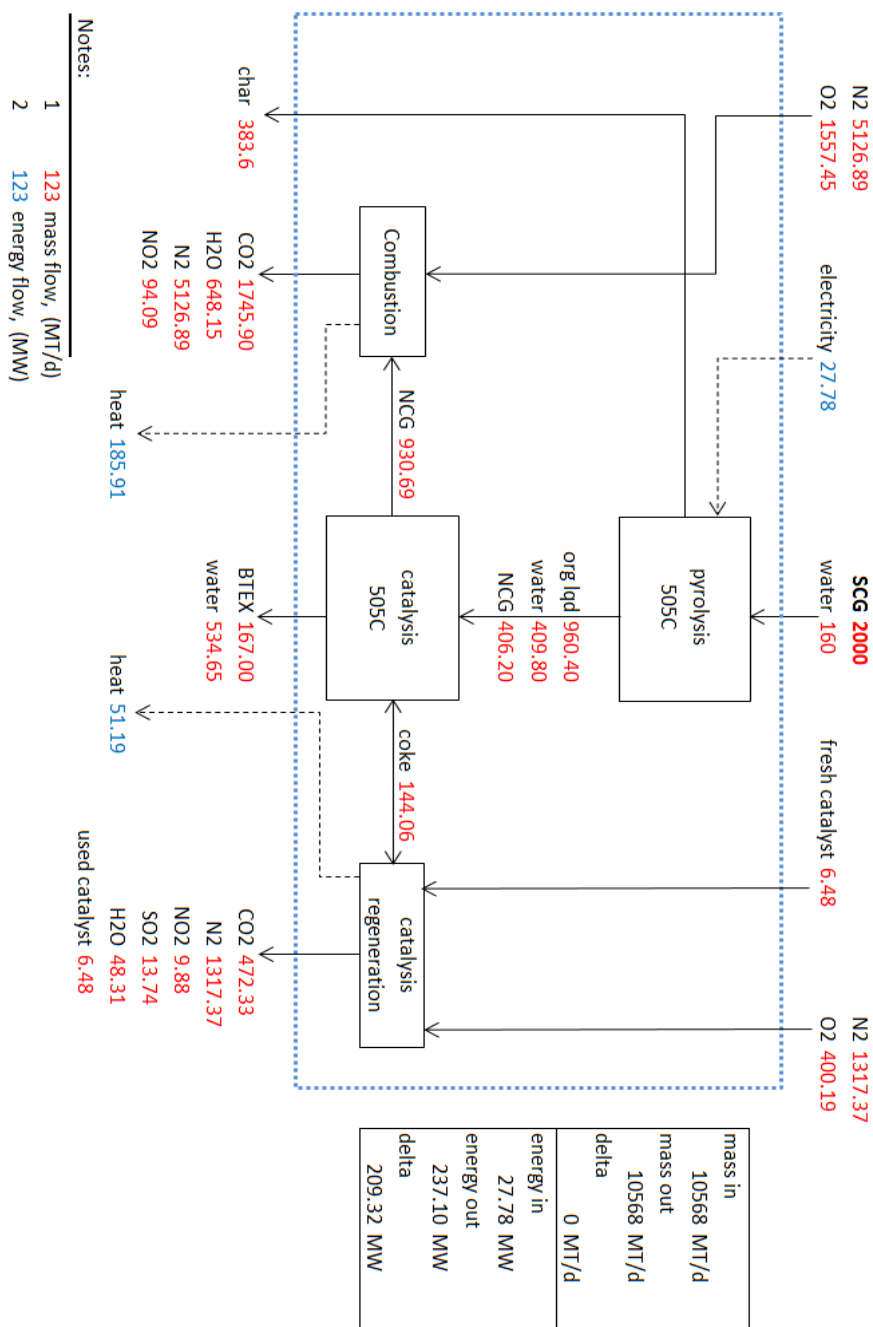


Figure 4.2 Mass and energy balance for the pyrolysis-catalysis process using spent coffee grounds as feedstocks.

4.2.3. Catalysis

Pyrolysis gas is fed to a fluidized-bed reactor (FBR) packed with a solid catalyst to produce BTEX-rich gas. The FBR designed for this proposed process is based on the design of industrial fluidized-bed catalytic cracking units. ZSM-5, a silica-alumina

zeolite, was selected as the solid catalyst because of demonstrated aromatics production using a wide array of feedstocks. ZSM-5 catalyst particle dimensions are assumed to have a 105 micrometer diameter and 0.6 sphericity for each catalyst particle. Bulk density of catalyst is assumed to be 680 kilograms per cubic meter. Catalyst deactivation is considered in the design, as chemical deposition of coke on catalyst active sites is known to increase costs and reduce profitability. ZSM-5 catalyst was assumed to remain active for 45 days, which is within the range of activity expected from actual fluidized catalytic cracking units used for petroleum operations. Deactivated catalyst is auger conveyed from the FBR to the catalyst regenerator, which reactivates the catalyst by combusting the coke. After reactivation, 20% of the catalyst, mainly fine material that has been significantly abraded, is discharged as spent catalyst. This is a sensitive assumption that must be verified by pilot trials, as fresh catalyst feed amounts to significant cost. Because of concerns over the scalability of existing reactor designs, this study assumes that ten 200 MT/day FBRs are employed in parallel. A four meter diameter cylindrical reactor was selected based on an entering gas volumetric flow rate of 1.85 cubic meters per second. Typically, a maximum height of ten meters is a limit for industrial scale fluidized bed reactors. Assuming a ten meter height, a volume of 128 cubic meters is computed for each reactor. To build a FBR with such size, an equipment cost of \$1.48 million (2011 \$) is required, thus ten reactors operating in parallel totals to \$14.8 million of capital cost.

4.2.4. Separation

Cyclonic separation of particulate biochar from pyrolysis gas follows fast pyrolysis. Design proceeded by establishing a cut diameter, which is the particle diameter corresponding to a 50% collection rate. Gas volumetric flow rate, entrained

particle size, number of spirals within the cyclone and gas velocity were used to determine the cut diameter as per Perry's Chemical Engineers' Handbook, 8th ed. Gas velocity was especially important for achieving a high collection efficiency of 98.7%. After sizing the cyclone, the equipment cost was found to be approximately \$1.26 million (2011 \$), a low value when compared to pyrolysis and catalysis equipment. As the screw-conveyor pyrolysis reactor does not use nitrogen, gas velocities may become unacceptably low for cyclonic separation. In this case, rotating particle separators (RPS) may be used to establish sufficient gas velocity to cause separation. Additional electric power is required to operate RPS, though this amount is expected to be low compared to catalyst costs. Cyclonic separation capital costs are similarly low for removing catalyst particles from the BTEX-rich gas product and from the flue gas created during catalyst regeneration.

4.4. Economic Analysis

An economic analysis of making green aromatics from biomass was conducted. The model consists of mass and energy balances, which were formulated using laboratory and pilot data when available; assumptions are stated for later verification, in the absence of data. Capital investment for each major equipment item was calculated using the standard method described in Peters and Timmerhaus. First, equipment was sized as per engineering design principles, and then capital investment was determined in the base year. Next, capital is inflated to 2011 dollars using cost indices that are regularly published in Chemical Engineering, the magazine, to determine equipment costs. Installed equipment costs are computed by multiplying the equipment cost by a Lang factor of 4.2. Table 4.1 contains a summary of the major capital costs for the proposed

process through BTEX-rich liquid production. An installed capital investment of \$177 MM dollars is required for converting 2,000 dry tons of biomass per day to 304 tonnes per day of BTEX-rich liquid using SCG as feedstock. Pyrolysis, catalysis, regeneration, and combustion are the major cost items in this analysis

Table 4.1 Capital cost estimates for the major process items needed for converting biomass to BTEX-rich liquid. A processing capacity of 2,000 tonnes of biomass per day, 90% on-line operation, and a Lang factor of 4 was used to determine total fixed capital investment.

Number required	Equipment Items	Equipment Unit Cost (MM \$)	Total Equipment Cost (MM \$)	Installed Cost (MM \$)
4	Rotary Dryer	0.68	2.72	10.88
10	Biomass Feeding Bin	0.02	0.24	0.96
10	Pyrolysis Reactor	1.27	12.74	50.96
20	Directed Heater	0.61	12.20	48.80
1	Biochar cyclone	1.26	1.26	5.04
1	Electrostatic Precipitator	0.30	0.30	1.20
10	Catalyst Fluidized-Bed Reactor	1.48	14.8	59.20
5	Catalyst regenerator	1.51	7.55	30.2
1	Catalyst Cyclone	1.08	1.08	4.32
1	Condenser	0.82	0.82	3.28
Total			53.71	214.84

Operating costs are functions of the mass and energy flows within the process. Variable costs, which vary with capacity on an annual basis, and fixed costs, which are invariant on an annual basis, are determined by the process model and presented in Table 4.2. Variable costs items include biomass, catalyst and utilities, such as natural gas, electricity and cooling water. Biomass is assigned a cost of \$15 per tonne in this model, under the assumption that spent coffee will require minimal transportation to the BTEX conversion facility. Catalyst is purchased at a cost of \$3,000 per ton, which is a significant cost, especially when the fresh catalyst feed stream is large. Natural gas was not needed as flue gases derived from uncondensed gas combustion and catalyst regeneration provide the necessary process heat. Cooling water was purchased at \$0.07

per 1000 tonnes, to account for the pumping and pipeline costs needed for delivery. Electricity was purchased at a rate of \$0.05 per kWh, which is a common rate for industrial-scale processes, though electricity was only used for process control which contributes a negligible amount to operating cost. The total variable costs are estimated to be \$1.218 per gallon of BTEX-rich liquid, with fresh catalyst being the single largest cost. For this reason, further catalyst research is recommended to reduce the purchase of fresh catalyst. Also, a valuation for excess biochar should be undertaken as power plants, water treatment plants, and soil amendments open potential markets that may justify a credit towards operating costs.

Table 4.2 Operating costs for SCG conversion to BTEX-rich liquid including both fixed and variable costs. Significant costs include catalyst, biomass, and depreciation.

Plant Capacity (tonnes dry biomass per day)	Stream factor	Plant Capacity (gal of BTEX per yr)	
2,000	0.90	16,524,545	
Fixed Capital Investment (M\$)			
214.84			
	Unit cost	Cost	Cost
Variable Costs	(\$/unit)	Units/Year	(\$/Year) (\$/gal)
SCG (tonnes)	15	657,000	9,855,000 0.596
Catalyst (tonnes)	3,000	2,746	8,238,780 0.499
Cooling water (1000 tonnes)	70	12,155	850,815 0.051
Electricity (MWh)	50	23,652	1,182,600 0.072
Subtotal of Variable Costs		20,127,195	1.218
Fixed Cost			
Operating Labor	(\$35/hour)	4,691,016	0.284
Maintenance Labor	(2% of Total Fixed Capital)	4,296,800	0.260
Supervision	(30% of Total Labor)	2,696,345	0.163
Benefits	(5% of Total Labor + Supervision)	584,208	0.035
Maintenance Materials	(2% of Total Fixed Capital)	4,296,800	0.260
Local Taxes and Insurance	(1.5% of Total Fixed Capital)	3,222,600	0.195
Depreciation	(20 yr straight-line, no salvage)	10,742,000	0.650
Subtotal of Fixed Cost		30,529,769	1.848
Total of Operating Cost		50,656,964	3.066

Fixed costs were also determined, though many assumptions were needed to

complete this portion of the analysis. Labor costs were divided into operating and maintenance labor. Operating labor was determined assuming two persons per shift at a rate of \$35 per hour and maintenance labor was assumed to comprise 2% of the total fixed capital investment. Supervision of labor was estimated to require 30% of the labor cost. Benefits were computed to be 5% of the total of labor and supervision. Maintenance materials and operating materials were 2% and 10% of the total fixed capital and labor costs, respectively. Local taxes and insurance were assumed to be 2% of the total fixed capital investment. Finally, straight-line depreciation was estimated assuming a 20 year service life with no salvage value. A total fixed cost of \$1.85 per gallon of BTEX-liquid was determined for this process, leading to a total operating cost of \$3.07 per gallon when using SCG as feedstock. Operating labor and supervision are especially significant, and whether the amounts selected by this design are needed should be further discussed.

4.5. List of Assumptions

- For reactor volume calculations, the ideal gas law was used to calculate catalyst contact time. A catalyst contact time of 10 seconds was used to obtain conversions which were found in the lab.
- During catalyst regeneration, the higher heating value of catalyst coke was assumed to be equal to the heat of combustion of coal.
- Catalyst activity is maintained at a constant rate.
- Catalyst deactivation and replacement in the fluidized bed is linearly extrapolated from the deactivation of catalyst in a fluidized catalytic cracking unit.
- The regeneration unit size was based on a catalyst retention time of 24 hours

- The gas flow rate into the combustor was assumed to be equal to the flow of gas into the reaction vessel, but composed of air.
- The fluidized bed reactor is isothermally operated at the designated operation temperature, and does not require cooling.
- Steel thickness in the fluidized bed reactor/regenerator is estimated at 2 inches.
- Fluidization height is assumed to be 2 times the packed bed height
- Cyclones in the system remove all solids
- The catalyst reactor is assumed to operate isothermally and exothermically, no heat is added
- The cost of electricity is \$0.05/kW.
- The cost of stainless steel used is \$5/kg
- The cost of catalyst is approximated at \$3,000/tonne
- The cost of cooling water used is \$0.26/1000 gallons
- 90% stream factor for all calculations
- Pressure drop will not be accounted for in the condenser or cyclone. Ample pressure is assumed to be created from the pyrolysis reactor to push the gas through these units.
- Depreciation is assumed to be 10% straight line over 20 years
- 90% collection of BTEX exiting the reactor was assumed in the process model

4.6. Conclusions

The techno-economic analysis of make green BTEX from spent coffee grounds was conducted. A total fixed capital investment equal to \$214 million was found necessary to purchase and install the necessary equipment, with a capable of 2,000

tonnes of biomass per day. This capital does not include the costs of utility and yard improvements or an amount for contingency. The total production cost of BTEX was estimated to be \$3.07 per gallon of BTEX.

Chapter 5 Integrating Torrefaction with Catalytic Pyrolysis to Make Green Aromatics

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A paper to be submitted to *Bioresource Technology*

5.1 Abstract

In the present study, the integration of torrefaction with catalytic pyrolysis to produce BTEX was investigated. Spent coffee grounds, a food waste, were used as feedstock to make aromatics. An economic analysis of this bioenergy system was conducted to examine BTEX yields, biomass costs and their sensitivities. Model predictions were verified experimentally using pyrolysis GC/MS to quantify BTEX yields for raw and torrefied biomass. The torrefaction severity was optimized to be 239°C and 34 minutes using the minimum production cost as the objective function. This optimization study found conditions that justify torrefaction as a pretreatment for making BTEX provided that starting feedstock costs are below \$58 per tonne.

Keywords: torrefaction; catalysis; pyrolysis; aromatics; biomass.

5.2 Introduction

Monoaromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylenes (BTEX), are widely used as additives to gasoline and precursors to polymers. Green aromatics from renewable biomass, as a substitute for aromatics from petroleum refining, are essential to reduce the dependence on petroleum and release of carbon dioxide. One green route for making aromatics from biomass is catalytic fast pyrolysis. Biomass can be converted into green aromatics catalytic pyrolysis at temperatures around 500°C, for a short resident time (less than 1 second) and with a high heating rate (larger than 1000 K/s) [73, 74]. Coffee, an important agricultural product, is consumed worldwide with a global

market of over 9 million tonnes per year [75]. U.S. food processing plants consume a large amount of coffee and produce 1.5 million tonnes of coffee waste every year [75]. Spent coffee waste is a form of lignocellulosic biomass that also has an oil content of around 15 wt% [76]. Many researchers have demonstrated the viability of using spent coffee to make green aromatics with HZSM5 as the catalyst [73, 77]. HZSM-5, a kind of crystalline aluminosilicate catalyst, capably accelerates the conversion of biomass into BTEX [31, 73]. However, biomass' high oxygen content is undesirable as it leads to high coke formation and low aromatic yields. Further, hauling bound oxygen is expensive, leading to poor economics in the supply chain.

Torrefaction is a pretreatment technology that upgrades the physicochemical properties of biomass. When biomass is heated in the absence of oxygen at temperatures between 200°C and 300°C, the oxygen content is lowered [12], a favorable event that benefits the production of renewable aromatic hydrocarbons from torrefied biomass. Torrefaction primarily degrades the hemicellulose in biomass, though the cellulose and lignin can undergo thermal cleavage and aromatization. It has been hypothesized that glycosidic bond cleavage occurs to break cellulose during torrefaction [78]. Such reaction would provide small molecules for aromatization during catalytic pyrolysis. However, severe torrefaction needs to be avoided because this can cause crosslinking, reduce aromatic yields and increase coke formation [79]. Hilton et al. demonstrated an appropriate torrefaction severity for reducing coke reduction, and increasing BTEX selectivity and yields on the weight of torrefied biomass [80]. Relative BTEX yields on torrefied biomass reduce the cost of transport and catalytic pyrolysis because the oxygen removed by torrefaction in biomass does not need to be transported and processed.

However, counter to enhanced yields on torrefied biomass, mass loss during torrefaction leads to lower overall yields which has been demonstrated [80, 81]. Further, capital and operating costs are increased because of the purchase and operation of the torrefier. Thus, in this study we hypothesized that a trade-off exists between the enhancement of relative BTEX yields on torrefied biomass and the reduction of overall BTEX yields.

Economic optimization studies for making green aromatics from torrefied biomass need to be conducted to obtain such metrics as the minimum BTEX production cost. This analysis is needed to determine whether BTEX from torrefied biomass at optimized conditions is superior to equally optimized BTEX directly from raw biomass pyrolysis and catalysis. To date, no such a study exists that makes this comparison. In this research, the effects of torrefaction on BTEX yields and production costs were studied. The optimized torrefaction severity was obtained by balancing the cost addition due to torrefaction with cost reductions in transport and catalytic pyrolysis. The economics of making BTEX from torrefied biomass were then compared with raw biomass to demonstrate whether the concept of integrating torrefaction with BTEX production is economically justified.

5.3 Method

5.2.1 Process description

Spent coffee grounds (SCG), a food waste, are used as feedstock to produce green aromatics. Figure 5.1 depicts the simplified process of using SCG to produce BTEX. SCG are collected at food processing plants. A centralized BTEX production facility, where catalytic pyrolysis reaction performs for making BTEX, is located among several food processing plants. Rotary dryers are used at food processing plants to dry SCG from

20 wt% to 5 wt% moisture content. In the untreated scenario, no torrefaction is required, so dried SCG are directly transported to the central conversion plant for making BTEX. In the torrefaction scenario, moving bed reactors are employed due to low maintenance and capital costs to perform torrefaction at food processing plants. The combustible off-gas that mainly contains CO₂ and CO, produced during torrefaction, is recycled and burned to heat the torrefier. The torrefied SCG are then transported by trucks to the central conversion plant.

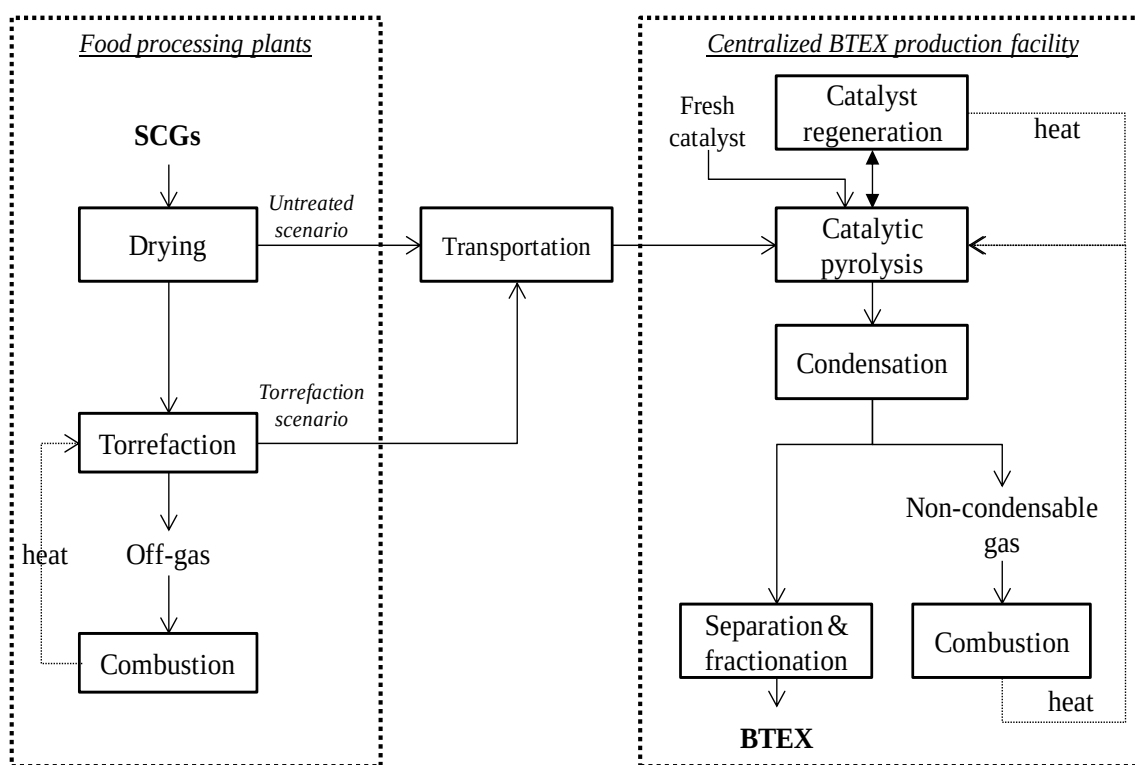


Figure 5.1. Generalized process flow diagram for converting SCG to BTEX.

At the centralized BTEX production facility, untreated or torrefied SCG are pyrolyzed in a fluidized bed reactor that is packed with solid catalysts to produce BTEX-rich gas. HZSM5, a silica-alumina zeolite catalyst, as it is known to be effective for cracking, deoxygenating and aromatizing cracking pyrolysis products [31, 73, 82]. Catalyst deactivation needs to be considered in the design, as chemical deposition of coke

on catalyst active sites is known to increase costs and reduce profitability. HZSM5 catalyst was assumed to remain active for 45 days, which is within the range of activity expected from actual fluidized catalytic cracking units used for petroleum operations. Deactivated catalyst is auger conveyed from the fluidized bed reactor to the catalyst regenerator, which reactivates the catalyst by combusting the coke. After reactivation, 20% of the catalyst, mainly fine material that has been significantly abraded, is discharged as spent catalyst. This is a sensitive assumption that must be verified by pilot trials, as fresh catalyst feed amounts to significant cost. The heat needed by catalytic pyrolysis is provided by the coke formed on spent catalyst and by combustion of the non-condensable gas co-product of pyrolysis. Next, BTEX-rich vapor is condensed and BTEX is separated and collected. Transportation of BTEX from the production facility to end users is not included in this study. The positive effects of torrefaction on BTEX production, such as high selectivity and catalyst coke reduction [80], were not considered in this study to simplify process optimization and economic analysis.

5.2.2 Model and experimental yields of BTEX from biomass

5.2.2.1 Experiment design

Both BTEX and torrefaction mass yields are functions of torrefaction severity. In order to formulate such functions, a central composite design (CCD) with two factors (torrefaction temperature and residence time) at five levels and three replicates at the center point, was employed to conduct experiments. A CCD is fractional factorial design that is supplemented with axial points to estimate curvature. Scopes of torrefaction temperature and residence time were set from 200 °C to 300 °C, and from 16 minutes to 50 minutes, respectively. A design of 11 groups of torrefied SCG with three replicates in

each group results in a total of 33 torrefied SCG samples. Another 3 untreated SCG samples were also prepared as the control group. A surface response model consisting of a quadratic polynomial regression, is expressed by equation (1) and was used to perform all predictions.

$$y = \beta_0 + \sum_{i=1}^2 \beta_i x_i + \sum_{i=1}^2 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j>i}^2 \beta_{ij} x_i x_j \quad (1)$$

Where y indicates the response factor (torrefaction mass yield or BTEX yields), x_i and x_j are independent variables that are torrefaction temperature and residence time. β_0 , β_i , β_{ii} , β_{ij} are intercept, linear, quadratic and interaction coefficients, respectively.

5.2.2.2 Biomass preparation and torrefaction

Fresh SCG were frozen and shipped from Coca-Cola Company in Atlanta. SCG were ground and sieved through a 60 mesh tray. Sieved SCG were dried in the oven at 60°C overnight and then stored in desiccators to maintain constant moisture content before the experiment. Torrefied SCG were made in a torrefaction furnace using nitrogen as a purge gas at a flow rate of 54 ml/min.

5.2.2.3 Catalyst preparation

ZSM5 catalyst with a silica–alumina ratio of 23 was calcined in air at 550 °C for 4 hours to obtain acidic HZSM5. ZSM5 in ammonium cation form was obtained from Zeolyst Co. (Conshohocken, PA). As measured by Zeolyst, the catalyst has a pore size of 0.6 nm, a pore volume of 0.14 m³/g and a surface area of 400 to 425 m²/g.

5.2.2.4 Catalytic pyrolysis

Torrefied SCG (or untreated SCG) and the catalyst were mixed at a weight ratio of 1:5. The mixed feedstock was then packed in a quartz tube where quartz wool and a

quartz filler rods were placed above and below the feedstock. A CDS Pyroprobe 5250 was employed to perform the catalytic pyrolysis. Samples in the pyroprobe were heated in the absence of oxygen at a temperature of 550°C with a heating rate of 999°C/s. The BTEX-rich vapors produced in the pyroprobe were blown by helium, as an inert transfer gas, to a Shimadzu QP-5050A gas chromatograph/mass spectrometer (GC/MS) to be analyzed. The transfer line was heated to a temperature of 300°C to avoid condensation of aromatics vapors. BTEX compounds were quantified using an external standardization method.

5.2.3 Economic analysis

5.2.3.1 Feedstock cost

SCG, as a food waste, were assumed to be collected at the food processing plant gate for a cost of \$15 per dry tonne. Biomass cost per tonne of torrefied SCG is a function of torrefaction severity as expressed in equation (2)

$$BC_{tor} = BC_{SCG} / Y_{tor}(time_{tor}, T_{tor}) \quad (2)$$

Where BC_{tor} is the biomass cost per tonne of torrefied SCG, BC_{SCG} is the biomass cost per tonne of untreated SCG that is \$15 per dry tonne. Y_{tor} is the torrefaction mass yield predicted using the surface response regression model in equation (1). Y_{tor} is a function of torrefaction temperature (T_{tor}) and residence time ($time_{tor}$).

5.2.3.2 Torrefaction cost

A longer residence time means that a larger torrefier is needed to produce the same amount of torrefied SCG. Thus, capital investment of torrefaction in this study was assumed to be an exponential function of residence time, as expressed in equation (3).

$$CI_{tor}(time_{tor}) = CI_{base} * time_{tor}^{0.6} \quad (3)$$

Where, CI_{tor} is the capital investment of torrefier at the required time. CI_{base} is the unit capital investment of torrefier at the base time of 30 minutes. $time_{tor}$ is the torrefaction residence time in minutes. A scale factor of 0.6 is assumed in this calculation, in accordance with the classical sixth-tenths rule.

5.2.3.3 Transportation cost

Semi-trailer trucks that have cargo capacities of 100 m^3 and 20 tonnes are employed to transport SCG from the food processing plant to the central conversion plant. The diesel consumption rate of such a semi-trailer was assumed to be 57 liters/km with full load and 35 liters/km with an empty load. Diesel was assumed to be purchased at a price of \$1 per liter, which is the U.S. average retail price in 2014. The actual cargo capacities of trucks are limited by either weight or volume depending on the bulk density of SCG. When the bulk density of torrefied SCG was larger than 200 kg/m^3 , the actual cargo capacity was determined to be 20 tonnes, otherwise 100 m^3 was used to calculate the cargo load. The bulk density of dried SCG was assumed to be 400 kg/m^3 , while the bulk density of torrefied SCG was calculated according to the mass loss during the torrefaction. It was assumed that torrefaction has very limited impact on the biomass volume in this calculation.

Transport cost mainly depends on the total travel distance and time. The average one-way travel distance from food processing plants to the central conversion plant was set to be 160 km. The total transport time includes the round-trip driving time, loading time and unloading time. The loading and unloading time for dry bulk material can be roughly estimated to be one minute for each cubic meter of volume [83]. The driving time was calculated assuming an average travel speed of 80 km/ hour.

5.2.3.4 Economics at the centralized BTEX production facility

For a given available amount of SCG, the more mass loss during torrefaction, the smaller capacity a centralized BTEX production facility (CBPF) would have. In the untreated scenario, an amount of 100 thousand tonnes of SCG per year was assumed to be available for a CBPF to be processed. In the torrefaction scenario, the capacity of CBPF was calculated by subtracting the mass loss during the torrefaction from the total available SCG in food processing plants. The labor cost at the CBPF, as a function of CBPF capacity, was scaled as a power function using an exponent of 0.25, as described by Peters et al. and Leboreiro et al. [67, 68]. All the capital investment for the main equipment at the centralized BTEX production facility were sized and inflated to 2014 USD using the chemical engineering plant index. The straight-line method was adopted in this study to estimate depreciation cost. Electricity price was assumed to be purchased at a price of 7.32 cents/kWh, which is the U.S. average industrial electricity price in 2014. The on-line time was set at 90%, which means that 10% of the time is used for maintenance and repairs. Total BTEX production cost at the CBPF gate, denoted as C_{CBPF} , was calculated by equation (4).

$$C_{CBPF} = FC + VC \quad (4)$$

Where, FC is the fixed cost of the untreated SCG scenario in which CBPF has a capacity of 100 thousand tonnes of SCG per year. VC is the production variable cost per tonne of feedstock, which involves costs of electricity, cooling water, fresh catalyst and labor.

5.2.3.5 Total BTEX production cost

The total production cost (TPC), as shown by equation (5), involves the biomass cost, drying cost, torrefaction cost, transportation cost, and the conversion cost at the CBPF. By dividing by Y_{BTEX} , which denotes the BTEX mass per mass of torrefied SCG, TPC is expressed in dollars per tonne of BTEX. Ten-thousand values of TPC at different torrefaction temperatures and residence times were calculated, from which the minimum TPC was obtained. The corresponding temperature and residence time were determined to be the optimized torrefaction severity.

$$\text{TPC} = (\text{BC}_{\text{tor}} + C_{\text{dry}} + C_{\text{tor}} + C_{\text{CBPF}})/Y_{\text{BTEX}} \quad (5)$$

5.4 Results and discussions

5.3.1 Prediction yields of torrefaction and BTEX

The torrefaction mass yields and BTEX yields at different torrefaction severities were collected upon experiment and are shown in Table 5.1, with the aim of fitting the statistical prediction model. BTEX yields in the table are on a weight basis of torrefied biomass. Untreated SCG, as the control group, results in a BTEX yield of 8.37%. The BTEX yield from torrefied SCG is higher than the control and grows with increasing torrefaction severity until a temperature of 285°C. Above this temperature, crosslinking in biomass may occur and cause a reduction in BTEX yields. The highest BTEX yields were observed around 250°C and 50 minutes.

The models to predict yields of torrefaction mass and BTEX were developed using the surface response regression model, and are shown in equation (6) and equation (7), respectively. Regression analysis shows high accuracy ($p < 0.05$, $R^2 = 98.73\%$) for predicting torrefaction mass yield, and acceptable ($p < 0.05$, $R^2 = 90.13$) to predict BTEX

yields. The prediction error of BTEX yields regression model is due to measurement errors of py-GC/MS and imperfect of regression model.

$$Y_{\text{tor}}(\%) = (4660 + 60.7T + 25t - 0.163T^2 + 0.628t^2 - 0.329T * t) * 10^{-4} \quad (6)$$

$$Y_{\text{BTEX}}(\%) = (-2915 + 32.05T - 0.73t - 0.0685T^2 - 0.09t^2 + 0.032T * t) * 10^{-4} \quad (7)$$

Table 5.1. Torrefaction mass yields and BTEX yields for SCG according to torrefaction severity. BTEX yield is expressed per weight of torrefied SCG.

Sample number	Torrefaction temperature (°C)	Residence time (min)	Torrefaction mass yield (wt %)	BTEX yield (wt %)
Control	untreated	-	100	8.37
1	200	30	96.30	8.57
2	215	16	95.57	8.71
3	215	44	94.26	8.87
4	250	10	92.19	8.85
5	250	30	84.96	9.51
6	250	30	84.98	9.48
7	250	30	85.07	9.53
8	250	50	83.02	9.63
9	285	16	77.25	7.61
10	285	44	69.49	8.39
11	300	30	65.73	7.20

5.3.2 Optimizing BTEX production cost

By balancing BTEX yields on the weight of torrefied biomass with of overall biomass, the torrefaction temperature and residence time were optimized to obtain the minimum BTEX production cost. Previous experimental research has demonstrated that torrefaction temperatures ranging from 240°C to 275°C provide the appropriate severity to positively affect BTEX production when using corncobs and loblolly pine as feedstocks [80, 81]. Economically, milder torrefaction severity is desired to avoid significant mass loss and the high biomass cost that results.

As shown in Figure 5.2, at a temperature of 239°C and a residence time of 34 minutes, BTEX production costs from torrefied SCG are minimized at \$1,271/tonne. For comparison, the untreated SCG scenario has a total production cost of \$1,423/tonne. This demonstrates that torrefaction is economical superiority versus untreated SCG, even though enhanced BTEX selectivity and catalyst coke reduction were not considered. Conversely, high torrefaction temperature and long residence time leads to severe mass loss and high biomass cost. As shown in Figure 5.2, when the torrefaction temperature is above 270°C, BTEX production cost increases steeply because of severe mass loss during torrefaction. Furthermore, a long residence time decreases the throughput of torrefiers and therefore increases their capital cost. In the area of low torrefaction temperature and short residence time, which represents insufficient torrefaction severity, BTEX production is not economical because BTEX yields (per torrefied biomass) are not enhanced enough to offset the increased costs of biomass and torrefaction.

Figure 5.3 (a) shows the effect of residence time on the BTEX production cost at the optimized torrefaction temperature of 239°C. At this temperature, a residence time ranging from 16 to 50 minutes always costs less than untreated scenario. Figure 5.3 (b) shows the effect of torrefaction temperature on the BTEX production cost at the optimized residence time of 34 minutes. At this residence time, a torrefaction temperature below 275°C has a lower total production cost than the untreated scenario. Overall, BTEX production cost is more sensitive to torrefaction temperature than residence time, so torrefaction temperature is the critical factor when balancing BTEX yields on the weight of torrefied biomass with on the weight of overall biomass.

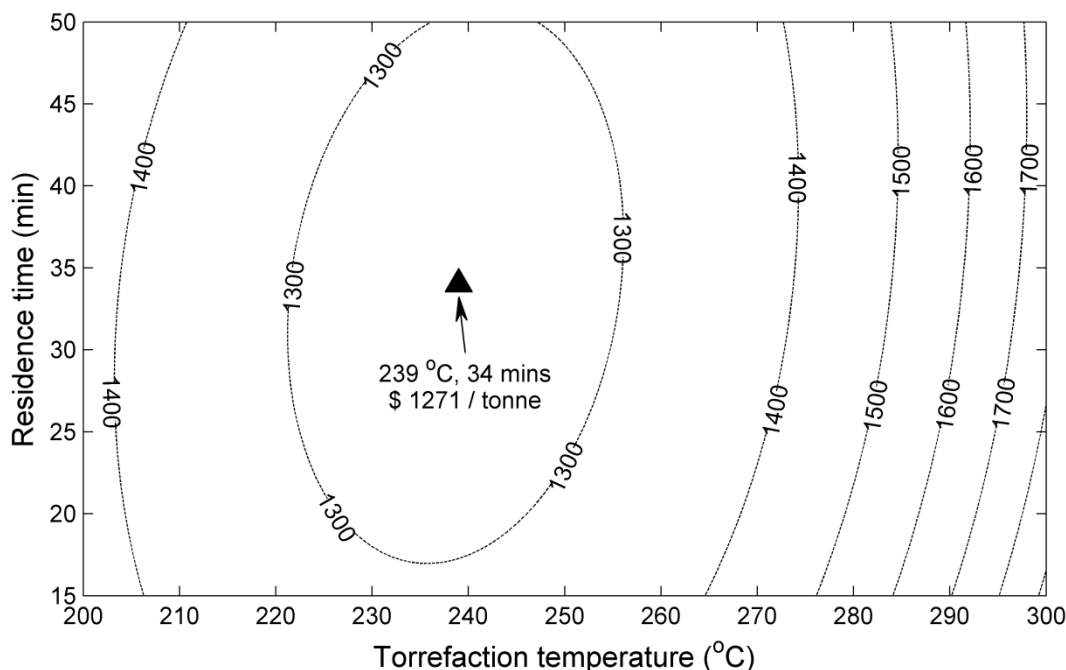


Figure 5.2. Contour plot of torrefaction severity vs. BTEX production cost.

5.3.3 Model verification

Table 5.2 Verification of regression model

	Torrefaction mass yield (wt%)	BTEX yield (wt%)	BTEX production cost (\$/tonne)
Prediction	84.32	9.56	1,271
Experiment	85.10	9.65	1,246

The regression models (equations 6 and 7) were verified by running the torrefaction furnace and py-GC/MS at the optimized torrefaction conditions (239°C, 34 minutes). As shown in Table 5.2, the torrefaction mass yield at the optimal conditions was tested to be 85.1% and 0.8% higher than the predicted value; the BTEX yield was tested to be 9.65% and 0.09% higher than the predicted value. The BTEX production cost calculated by experimental yields is \$1,246 per tonne of BTEX, and is \$25 lower than the prediction value by model. Those results show the regression models can predict the yields of torrefaction mass and BTEX with reasonable accuracy.

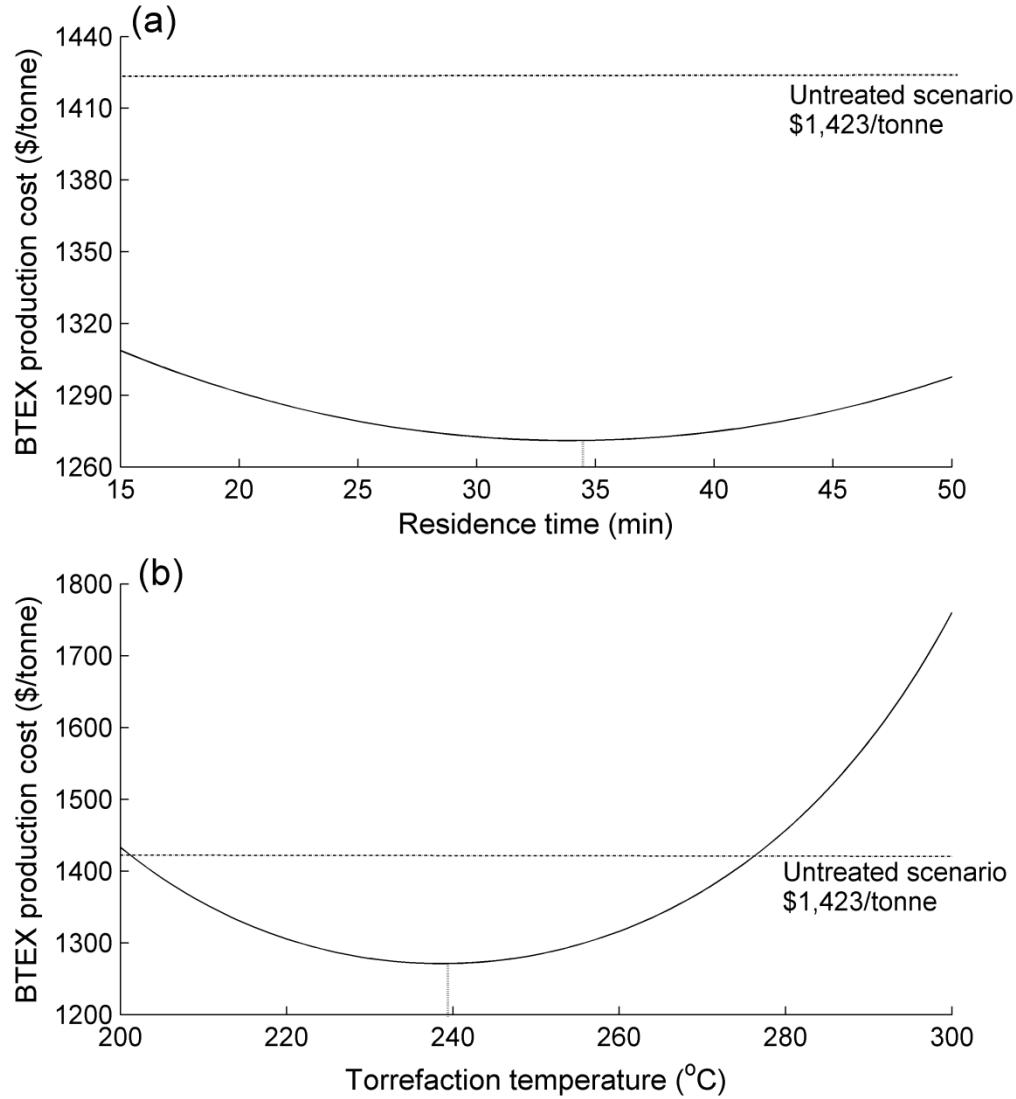


Figure 5.3. Plots of (a) residence time vs. BTEX production cost at the optimized torrefaction temperature (239°C); and (b) torrefaction temperature vs. BTEX production cost at the optimized residence time (34 mins).

5.3.4 Effects of transport distance and biomass cost

Two factors, including the average transport distance from food processing plants to the centralized BTEX production facility and the biomass cost at the food processing plant gate, were selected for sensitivity analysis on BTEX production costs. Both distance and biomass cost were varied by $\pm 100\%$, which results in a range of 0 to 320 km for distance, and a range of 0 to \$30 per dry tonne for biomass cost.

According to Figure 5.4, transport distance is more sensitive than biomass cost for both torrefied SCG and untreated SCG scenarios. The effect of transport distance is especially significant on the untreated scenario because the high oxygen content in raw biomass lowers the transport efficiency. If transport distance equals zero, which means BTEX is produced at the food processing plant, the torrefied SCG and untreated SCG scenarios have the lowest and very similar BTEX production costs of around \$1,000/tonne. However, in reality, a large BTEX production facility, which is served by multiple food processing plants, benefits from economies of scale. At longer transport distances, the torrefaction scenario exhibits cost savings versus the untreated scenario. Thus, when long distance transportation of SCG is needed (e.g. oversea shipping), torrefaction greatly reduces the total BTEX production cost by reducing oxygen content and thus enhancing transport efficiency. According to Figure 5.4, when biomass cost rises, the torrefaction scenario's BTEX cost increases more steeply than untreated scenario because mass loss during torrefaction increases the total production cost. The intersection point of these two lines occurs at a biomass cost of \$58 per dry tonne. Thus, when the biomass cost goes above \$58/tonne, the untreated scenario (i.e. no torrefaction) should be chosen for making BTEX.

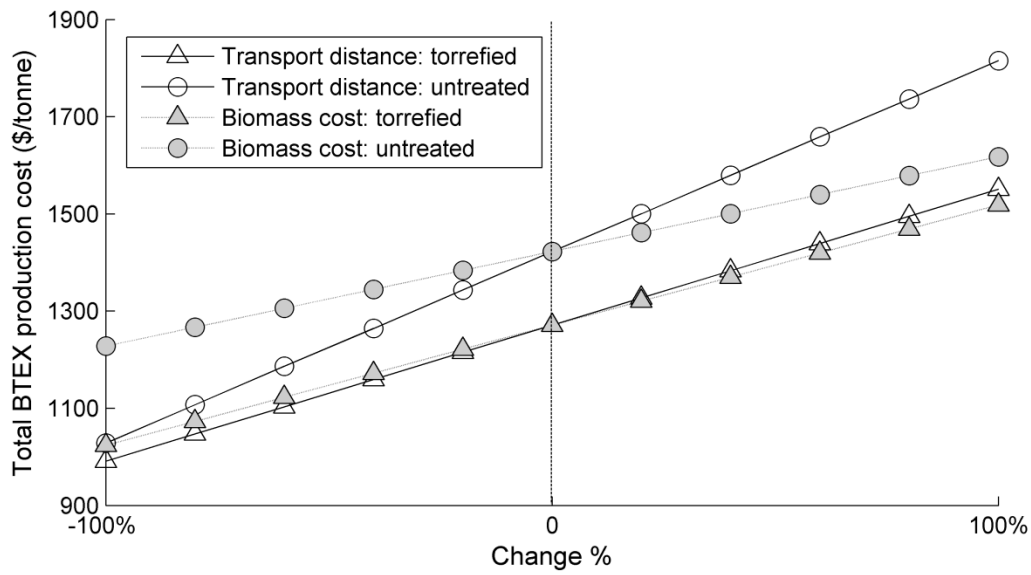


Figure 5.4 Effects of transport distance and biomass cost on BTEX production costs.

5.5 Conclusions

The optimal torrefaction severity (239 °C and 34 minutes) was determined to obtain the minimum total BTEX production cost. Comparing the BTEX cost from untreated SCG (\$1,423/tonne), torrefaction is justified for the optimized scenario (\$1,271/tonne). The effects of transport distance and biomass cost on BTEX production cost were studied. With a long biomass transport distance, torrefaction is strongly recommended to preprocess biomass into a form with low oxygen content to increase transport efficiency. When the biomass cost is larger than \$58/tonne, the torrefaction scenario is not an economical option to produce BTEX, because mass loss during torrefaction results in a high total production cost.

Chapter 6 Conclusions and Future Work

6.1. Conclusions

To justify the economics of integrating decentralized biomass upgrading depots (BUDs) with a centralized aromatics production facility, aromatics production from torrefied biomass was investigated. Py-GC/MS results show the torrefaction can enhance BTEX yields on the weight of torrefied biomass at an appropriate torrefaction severity. Using torrefied spent coffee grounds (SCG) as feedstock to make BTEX, the optimal torrefaction severity (239 °C and 34 minutes) exists and results in a total production cost of \$1,271 per tonne, comparing with a cost of \$1,423 per tonne with untreated SCG as feedstock. The effects of transport distance and starting biomass cost were also studied. Results show that torrefaction benefits BTEX production economics a lot when biomass is required to be transported for a long distance. This is mainly due to the reduction of biomass's oxygen content saves the transport cost. However, when the starting feedstock cost goes up to \$58 per tonne, torrefaction was not economical to upgrade biomass as mass loss during the torrefaction results in a high biomass cost. The economics of BUDs were also studied. The process variables, such as biomass on site drying time and depot size, were optimized. The effects of weather conditions on BUDs reveal that torrefaction is more worth to be implemented in the humid region, because the off-gas, a by-product during torrefaction, can be combusted to provide energy and thus save drying cost. Overall, based on the results in this dissertation, the process integrating BUDs with a centralized bio-refinery was justified.

6.2. Future work

For the further study of integrating BUDs with catalytic pyrolysis to make aromatics, the following work should be conducted in the future:

- The effects of torrefaction severity on BTEX selectivity, coke yield, and catalyst performance should be examined deeply.
- Various feedstock and catalysts should be investigated to study the effects of torrefaction on aromatics production.
- The capacity of centralized bio-refinery should be optimized to further lower the BTEX production cost.
- Life-cycle assessment should be conducted.

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