Trends in Chemical Engineering
Vol. 21, 2023

Original Article

# A process for producing vanillin and co-products from corn stover lignin

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## ABSTRACT

A key strategy for combating global climate change is reducing the use of fossil carbon resources such as petroleum and coal. Fossil carbon is the primary raw material used in many fuels, chemicals, and polymeric materials and is also a primary raw material for the production of many food flavorants such as artificial vanilla. One potential replacement resource is lignin. Lignin is a large complex polymer with an abundance of cyclic groups making it a good candidate to produce chemicals that typically come from crude oil. However, the transformation of lignin into these compounds is a challenge, and processes to use lignin as a crude oil substitute have yet to be commercialized. Lignin is present in woods, grasses, and other lignocellulosic plants, including corn. Corn is North Dakota's third most profitable crop and a popular crop throughout the world. Most of the corn's stover is underutilized, making it a potentially cheap and renewable source of lignin. In this study, a novel process was developed based on a unique non-catalytic decomposition technology developed at the University of North Dakota to decompose lignin into valuable monomers that can be recovered and purified into valuable products. A preliminary design was completed at the process flow diagram level with a focus on the production of vanillin, a common and valuable flavorant, along with other useful co-products. The design was used to develop an American Association of Cost Engineers (AACE) Class 4 factored capital cost estimate and comparable operating costs and revenue estimates to evaluate process feasibility. At a commercial-scale design feed rate of 3,300 kg/hour of corn stover-derived lignin, the designed process has a projected net present value at a hurdle rate of 20% (NPV@20%) of $51 million and a discounted cash flow rate of return (DCFROR) of 35%, indicating that it is likely to be commercially viable.

**KEYWORDS:** lignin decomposition, renewable vanillin, corn stover lignin, techno-economic analysis.

## 1. INTRODUCTION

Around the world, increasing efforts have been placed on reducing the global carbon footprint. The United States (US) Department of Energy has committed to net-zero carbon emissions by 2050 and the US has rejoined the Paris Agreement [1]. For the US to be compliant with the standards set by the agreement for 2030, carbon emissions must be cut by half [2]. To achieve this goal, a transition from fossil fuels to more sustainable clean energies is required as fossil fuels account for 93% of the greenhouse gas emissions in the US [3].

Fossil fuels are used for more than just fuel. Fossil fuels are also used in the formation of compounds such as plastics, carbon fiber, platform chemicals, flavorants, etc. [4]. As the world transitions to

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clean energies and fossil fuels become obsolete, a new, renewable source of carbon must be identified and utilized to replace fossil fuels in the formation of petroleum-based products. One of the most promising sources of carbon that can replace fossil fuels is biomass due to its renewability and abundance. One such biomass of interest is corn stover.

Corn stover is a lignocellulosic material that consists of the leftover stalks, leaves, husks, and cobs from the corn harvest [5]. Most of the corn stover generated is used to return nutrients to the soil after harvest, but excess corn stover can be used as a carbon source. In general, up to 50 wt% of corn stover produced can be harvested without affecting the next crop's yield, although in certain soils, farmers may not want to harvest crop residue every year. Further, based on environmental conditions, extra corn stover may need to be left in the field to account for erosion [5]. Corn stover mainly consists of cellulose (~35% w/w), hemicellulose (~20% w/w), and lignin (~12% w/w) [6]. Cellulose and hemicellulose can be converted to sugars, for example, through the use of acid hydrolysis and enzymatic hydrolysis. The conversion of these sugars into useful platform chemicals and biofuels has been heavily studied [7-10]. Although just as heavily studied, there has been less success in identifying ways to convert the lignin portion of the corn stover into useful fuels or chemicals. Currently, in most lignocellulosic processes, lignin is underutilized and treated as a waste stream or low-grade burner fuel [11].

Finding a reliable method to produce useful chemicals from lignin has the potential to add a higher value revenue source for lignocellulosic biorefineries, making them economically viable while also providing a renewable pathway for fuels, chemicals, and other products such as the flavorant vanillin. The goal of the research reported herein is to evaluate the technical and economic viability of using a novel in-house-developed lignin decomposition method to valorize lignin. The study also focused on identifying attractive potential end-products from the lignin fragments generated during the decomposition.

Lignin is an abundant complex organic polymeric macromolecule present in the cell walls of nearly all plants. It is insoluble in water but becomes more soluble as temperature increases. Although it is essentially insoluble in water at room temperature, lignin becomes very soluble in basic aqueous solutions at a pH of 10 or higher. Lignin is composed mainly of three monomeric units called monolignols: p-coumaryl alcohol (a p-hydroxyphenyl unit often denoted as H type), coniferyl alcohol (a guaiacyl unit often denoted as G type), and sinapyl alcohol (a syringyl unit often denoted as S type) [12]. Lignin is responsible for giving a plant its rigidity and resistance against environmental attack [13]. It is present in different plants in different amounts and in different forms. Something rigid, like wood, tends to have more lignin than something like grass.

The structure of lignin is complex and diverse, so an exact structure is not known. Still, lignin can be divided into three distinct groups based on similar properties and plant taxonomy: grass or lignocellulosic (LC) lignins, softwood lignins, and hardwood lignins [12]. Softwood lignins have a significant concentration of guaiacyl groups (often 95% or more) while having no S type units with the remainder being H type units, whereas hardwood lignins are mostly a mixture of syringol (47-75%) and guaiacyl groups (25-50%) with the remainder being p-hydroxyphenyl groups (0-8%). Grass lignins contain significant amounts of all three major groups of monolignols (G type: 35-80%, H type: 5-35%, S type: 20-55%) [14]. The monomeric units can be connected by many different linkage types; however, β-O-4 linkages are the most prevalent linkages in lignin and are relatively weak linkages compared to others, making them the primary target of most degradation processes [15]. LC lignins, such as the lignin in corn stover, also vary in composition and have been less heavily studied compared to hardwood and softwood lignins.

Many methods have been proposed for lignin decomposition, but so far, none have been proven to be both technically and economically viable. One complication is lignin's complexity which makes it difficult to characterize. In addition to many decomposition methods, many different pretreatment methods have also been proposed, such as milling, organosolv, and alkaline pretreatment methods [16]. These pretreatment methods have been proposed to reduce the recalcitrance of lignin and increase the yield of useable decomposition products. They also are used to separate the lignin from the cellulose, making it easier to break down for use [17]. In the end, not much can be said with certainty concerning the structure and decomposition of lignin, and despite 50+ years of research, the understanding of decomposition still has many unknowns.

Hydrothermal treatment refers to a general class of processes in which biomass is dissolved or slurried with water and then treated at high temperatures. Most commonly, this technique is used to facilitate a chemical reaction. Both approaches – dissolution and slurry – have been studied for lignin decomposition. These decomposition reactions include ionic and free radical-type reactions. Ionic reactions are favored at subcritical conditions, while radical reactions are favored at supercritical conditions [18]. The products of these decomposition reactions typically include char, non-condensable gaseous species (carbon monoxide, hydrogen gas, methane, carbon dioxide, etc.), water-soluble polymers, phenolic compounds, cyclic hydrocarbons, and aromatic hydrocarbons. A higher conversion to the most useful compounds is generally achieved at supercritical conditions rather than sub-critical. Unlike other decomposition methods, cleavage of C—C bonds, alkylation, deoxygenation, and repolymerization occur nearly simultaneously while leaving the benzyl rings relatively unaffected. Reaction temperature, residence time, and heating rate appear to be the most important factors when determining yield [19]. Products of this type of reaction vary based on the type of lignin used and the pretreatment method. Hydrotreating methods can be used to produce organic acids, bio-oils, and phenolics. The aromatic rings themselves are mostly unaltered using this method of decomposition [20]. The major phenols produced are phenol, catechol, guaiacol, and cresols [21].

Hydrothermal treatment under basic conditions (pH above 10) is employed to facilitate lignin dissolution in an aqueous solution. It has been shown that at basic, subcritical conditions, lignin decomposes to target compounds at yields (≈20 wt%) that are similar to those achieved at supercritical conditions (≈34 wt%) without base addition but at the expense of more char formation in catalytic decomposition reactions [18, 22, 23]. As a consequence, hydrothermal lignin decomposition under basic conditions is less energy intensive. In addition, basic conditions also decrease the yield of less valuable oligomers and increase the yield of the more valuable monomer products. Products of this type of reaction vary based on the type of lignin used and the pretreatment method. The products of hydrothermal decomposition under basic conditions are much the same as those achieved by hydrothermal decomposition under neutral or acidic conditions, except that the yield of phenolic products is much higher compared to that of bio-oils and organic acids [24].

The experimental results used in the current study were obtained using the hydrothermal base-facilitated decomposition of corn stover lignin. Documentation of the details of these experiments and the results is outside of the scope of the current study. The data utilized were based on a 16.6 wt% (inlet carbon basis) conversion to monomeric products with high concentrations of guiacols and phenols.

Guaiacol is a colorless oil that naturally occurs in many plant leaves and seeds, as well as wood smoke [25]. Guaiacol is mainly used as an intermediate to other chemicals. Since it is a compound that can be derived from biomass, it has been studied for its potential to produce green fuels. Commercially, guaiacol is a precursor to flavorants and expectorants, antiseptics, and local anesthetics [26]. Over 85% of the world's demand for vanilla is satisfied by the production of vanillin from guaiacol collected from the oil industry [27]. By using biomass as the source for guaiacol, reliance on fossil fuels for compounds like guaiacol and vanillin can be reduced.

Vanillin is a phenolic aldehyde that appears as white needle-like crystals at room temperature. Vanillin is mainly used as a flavoring agent in foods, drinks, and pharmaceuticals. Vanillin has a strong vanilla flavor and is the main flavoring component in both natural and artificial vanilla.

In fact, it is the only flavoring agent in artificial vanilla. Artificial vanilla makes up to 99% of all vanilla sales worldwide, and over 85% of that vanillin is produced from one of two petrochemicals derived from crude oil, eugenol and guaiacol. The remaining fraction of vanillin is produced from sulfonated lignin, a wood pulp industry byproduct [28].

The most common industrial process to produce vanillin is known as the Riedel process which converts guaiacol into vanillin. However, this process can also be started from common chemicals like phenol and catechol by first converting them to guaiacol. The process includes two reaction steps. The first reaction is a condensation reaction using guaiacol and glyoxylic acid at roughly a molar ratio under basic conditions to produce vanillylmandelic acid. This reaction is favorable because it is highly selective and avoids side reactions that lead to increased separation costs. The concentration of glyoxylic acid mainly controls the yield, and yields reach around 74% based on glyoxylic acid. The most significant side reaction is the formation of glycolic acid due to the presence of glyoxylic acid in basic conditions. The second reaction is the oxidative decarboxylation of vanillylmandelic acid to form vanillin. This reaction is usually carried out using a copper(II) catalyst and an aqueous alkaline medium at a temperature of 80 to 130 °C with a yield of around 88% based on vanillylmandelic acid [27].

The global market for vanillin is expected to be worth about $740 million (US) by 2026. The demand for vanillin is approximately 20,000 tons per year and growing with a compounding annual growth rate of 7.1% [29]. 'Natural' vanilla usually means that the product contains oils extracted from a vanilla bean. However, due to labeling regulations, vanillin produced using microorganism-based reactions can also be labeled as natural. This has caused many companies to invest heavily into studying these approaches, as artificial vanilla has a value of $10-20/kg, while natural vanilla is worth hundreds to a couple thousand dollars per kilogram. In addition, biological and lignin-based reactions can produce ethyl vanillin in addition to vanillin. Ethyl vanillin is considered to have a richer and stronger flavor profile than vanillin, adding value to the product [28].

## 2. MATERIALS AND METHODS

### 2.1. Design

A preliminary design was completed for all unit operations down to the size of a pump at an accuracy of +/-30%. The process was documented using an input/output (I/O) diagram, block flow diagrams (BFDs), and process flow diagrams (PFDs) using preliminary design approximation techniques and ASPEN Plus process simulation software. Equipment was sized using an in-house methodology facilitated by the ASPEN Plus™ process simulation application. Utility and consumable chemical requirements were also estimated. Summary information is provided in this article. The complete information is available in reference [30].

### 2.2. Economics

An in-house method was used to develop an AACE Class 4 factored broad capital cost estimate [31]. Equipment costs were estimated using cost charts developed by Ulrich and Vasudevan [32] or using the equipment cost estimation feature of ASPEN Plus. Estimating factors were used to adjust for higher costs associated with high pressure and materials of construction as appropriate. A direct cost factor was applied based on the unit operation type to account for installation, piping, instrumentation, electrical, and other cost elements directly associated with that piece of equipment. Summary information is provided in this article. The complete information is available in reference [30].

As a grassroot project, 30% of the total module cost was estimated to account for additional direct costs, such as utility and storage facilities, to yield a total direct cost. The total indirect costs were estimated as 25% of the total direct cost. Initial working capital was estimated as 10% of the total indirect costs. The sum yields the estimated fixed capital investment (FCI) requirement. Additional capital costs were included to account for the costs for catalysts and chemicals and working capital. The costs for catalysts and chemicals were estimated by calculating the cost of the estimated initial charge of chemicals and catalysts. Working capital was estimated as 10% of the FCI. The sum of these elements yielded the total capital investment (TCI) requirement.

The unit prices of all products, raw materials, chemicals, and catalysts were calculated based on their historical price trend at the basis date of August 2020. When price history was unavailable, spot prices were used. The following additional operating expenses were estimated: operating labor, maintenance, utilities, wastewater treatment, and general allocated expenses all at a comparable level of accuracy as the capital costs. Utility costs were calculated for steam, cooling and boiler feed water using in-house rules of thumb.

Profitability was calculated using a cash flow sheet method with an assumed facility economic life of 20 years. The fixed capital investment was spread across the project development schedule which was estimated as two years (Years -1 and 0). Initial chemical and catalyst expenses and working capital were applied immediately before operation (Year 0) and the working capital was refunded as a credit in the final year (Year 20). US income tax requirements were estimated by calculating the gross profit (revenue less the operating costs). Depreciation based on a 17 year modified accelerated cost recovery system (MACRS, full year convention) of the fixed capital investment was subtracted from the gross profit for each year of operation, yielding the federal taxable profit. Federal taxes were applied at the 2020 rate of 21%. State taxable profit was calculated as the federal taxable profit less the federal income tax. State tax was applied at the 2020 South Dakota rate of 0% [33]. Net profit after process commissioning (Years 1-20) was calculated as gross profit minus federal and state taxes. Annual net profits were discounted to year 0 using a hurdle rate (discount factor) of 20%. The NPV@20% was calculated as the sum of the discounted net profit of each year and the DCFROR was calculated by finding the hurdle rate at which the NPV@DCFROR=$0.

### 2.3. Design assumptions

1. The process was designed assuming it would be part of a grassroot plant with a 20 year economic life.
2. Designed processes have an operating factor of 95%.
3. Reaction 1 conducted in the Lignin Hydrothermal Reactor (R-102) has a conversion of 16.6 wt% of lignin to monomers and with 58.6 wt% unreacted lignin remaining in solution with a residence time of 10 min.
4. The balance of lignin in reaction 1 (42 wt%) is converted to syngas (Syngas composition in wt%: CO 43, $CO_2$ 14, $H_2$ 35, $CH_4$ 7.4).
5. Unreacted lignin recycled to the Lignin Hydrothermal Reactor (R-102) can be broken down to monomer products.
6. Monomers recycled to R-102 are inert.
7. Reaction 2 conducted in the VMA Reactor (R-302) has a residence time of 30 min and a conversion of 58 wt% guaiacol.
8. Reaction 3 conducted in the Vanillin Reactor (R-341) has a residence time of 30 min and a conversion of 88 wt% of VMA.
9. Distillation tray efficiency: 70%.
10. Pumps operate at 70% efficiency.
11. Compressors have a polytrophic efficiency of 65%.
12. Conveyor efficiency: 85%.
13. Mixing motor efficiency: 85%.
14. D-323, Toluene/Water Phase Separator and D-353, Water/EA Phase Separator are assumed to reach perfect phase separation; VMA and glyoxylic acid separate according to literature [34, 35].
15. Glyoxylic acid will not disproportionate under operating conditions and is recyclable.
16. Hold up time in all reflux drums, KO drums, mixers and settlers is 450 s.
17. The height-to-diameter ratio used for reflux and hold up drums is 3:1.

18. Distillation columns were sized with sieve trays at a spacing of 0.3 m.
19. Mist eliminators have a pressure drop of 20 kPa.
20. There is a 70 kPa drop in pressure for every 4 m of packing in packed columns.
21. There is a 0.7 kPa pressure drop for every tray in trayed columns.
22. Thermosyphon reboilers have a pressure drop of 1 kPa for the return vapor and 20 kPa for the bottoms' stream without a transfer pump due to the anticipated control valve in the bottoms stream.
23. High pressure steam is available at 258 °C and 4.48 MPa.
24. Boiler feed water is available at 38 °C and 0.538 MPa.
25. Cooling water is available at 20 °C and 0.414 MPa.
26. Molten salt (potassium nitrate and sodium nitrate) is available at 565 °C and 0.345 MPa.

### 2.4. Economic assumptions

1. Federal tax rate: 21%
2. South Dakota corporate income tax: 0%
3. Project economic lifetime: 20 years
4. Hurdle rate: 20%
5. Depreciation schedule: 17 years
6. Vanillin can be sold at a 15% premium due to its green feed source compared to current artificial vanillin products.
7. Annual maintenance costs are 4% of the FCI.

## 3. RESULTS AND DISCUSSION

### 3.1. Process design

The process was designed to a capacity of 3,300 kg/hour of corn stover-derived lignin. The process produces 280 kg/hr phenol, 29 kg/hr creosol, 140 kg/hr syringol, 77 kg/hr of acetovanillone, and 310 kg/hr vanillin.

The process is separated into four process areas. Simplified process flowsheets are shown in Figures 1-6. Process area 1 preps the lignin for reaction, decomposes the lignin, and extracts the products from the reaction solvent, water. Process area 2 separates and purifies extracted monomer products *via* high-temperature distillation. Process area 3 takes the guaiacol produced in process area 1 and purified in process area 2 and converts it to vanillin product. Process area 4 is a fired heater used to heat molten salt utility and generate utility steam.

In process area 1, solid lignin is dissolved in an aqueous solution of NaOH. The solution is pressurized and heated to 250 °C and 14.25 MPa and then routed to the lignin decomposition reactor. The reactor outputs monomeric products, syngas, and unreacted lignin. The syngas is separated off using a series of flash drums. Monomeric products are extracted using ethyl acetate as a solvent. Unreacted lignin, NaOH, and water are recycled. A distillation column separates the ethyl acetate from the monomeric products. The ethyl acetate is recycled and the monomeric products are routed to process area 2.

In process area 2, a train of distillation columns separates and purifies products in order of volatility. Separated guaiacol is sent to process area 3.

In process area 3, guaiacol is routed to a reactor where it is combined with NaOH, water, and glyoxylic acid. The guaiacol and glyoxylic acid undergo a condensation reaction to produce vanillylmandelic acid (VMA), a precursor to vanillin. The reaction is aided by a basic environment. The stream is neutralized and unreacted reactants are separated from the VMA intermediate using toluene. The reactants and toluene are separated and recycled *via* distillation. VMA is routed to a reactor along with NaOH and water. The VMA undergoes a decarboxylation reaction producing vanillin product. The reaction is aided by a CuO catalyst, a basic environment, and available oxygen. The stream is neutralized and both reactants and products are extracted using ethyl acetate (EA). EA, vanillin, and VMA are separated from each other in order of volatility by distillation. EA and VMA are recycled.

In process area 4, a direct-fired heater is fed syngas, natural gas, and air. The heat produced

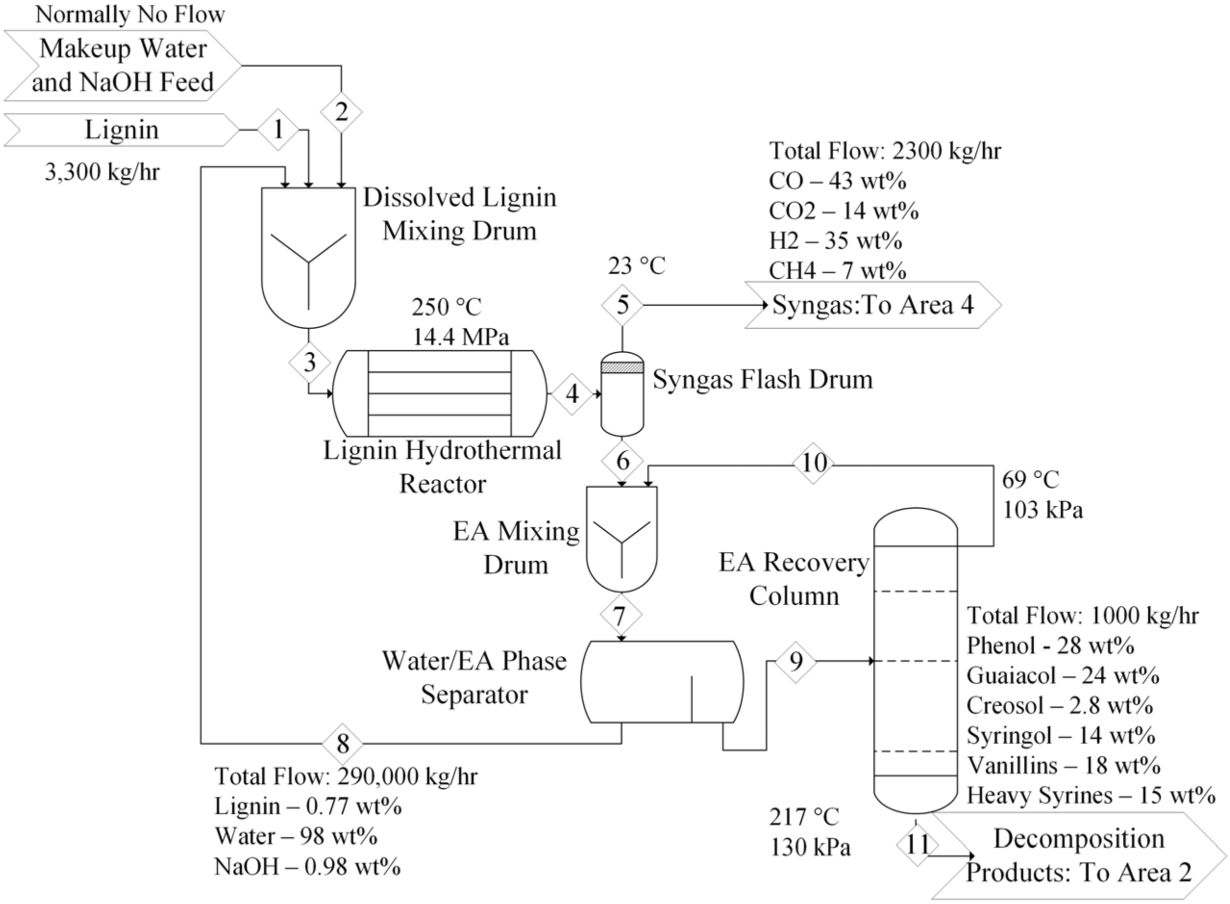

**Figure 1.** Simplified process area 1. EA = ethyl acetate (mass balance may not sum due to rounding).

from the fired heater is used to heat up the molten salt utility. Excess energy is recovered in an economizer section by producing low-pressure and high-pressure saturated steam utilites.

### 3.2. Capital costs

The AACE class 4 [31] capital cost summary for the designed process and a summary of equipment costs can be seen in Table 1. The cost for each piece of equipment was found by calculating an unadjusted purchase cost for each piece of equipment. This was done through the use of the Aspen Plus process simulator and the cost charts published by Ulrich and Vasudevan [32]. The unadjusted purchase cost was then modified by appropriate factors according to the material of construction, basis date, pressure, and type of equipment. The designed process has 111 pieces of equipment. After applying the applicable factors and considering the desired number of units, the total line item cost was calculated. The line item costs were then summed to find the total direct line item costs ($40 million).

Estimating factors were used to calculate the additional direct costs that come with grassroots projects. For a grassroots project the cost of purchasing land, pipeways, auxiliary areas such as utilities and raw material/product storage, other supporting facilities, and control room costs are considered. These additional direct costs are estimated to be 30% of the total line item costs ($12 million). The sum of the total line item costs and the additional direct costs yields the total direct cost ($52 million). The indirect costs are estimated to be 25% of the total direct cost ($13 million). The sum of the total direct cost and the indirect cost yields the fixed capital investment ($65 million). The initial

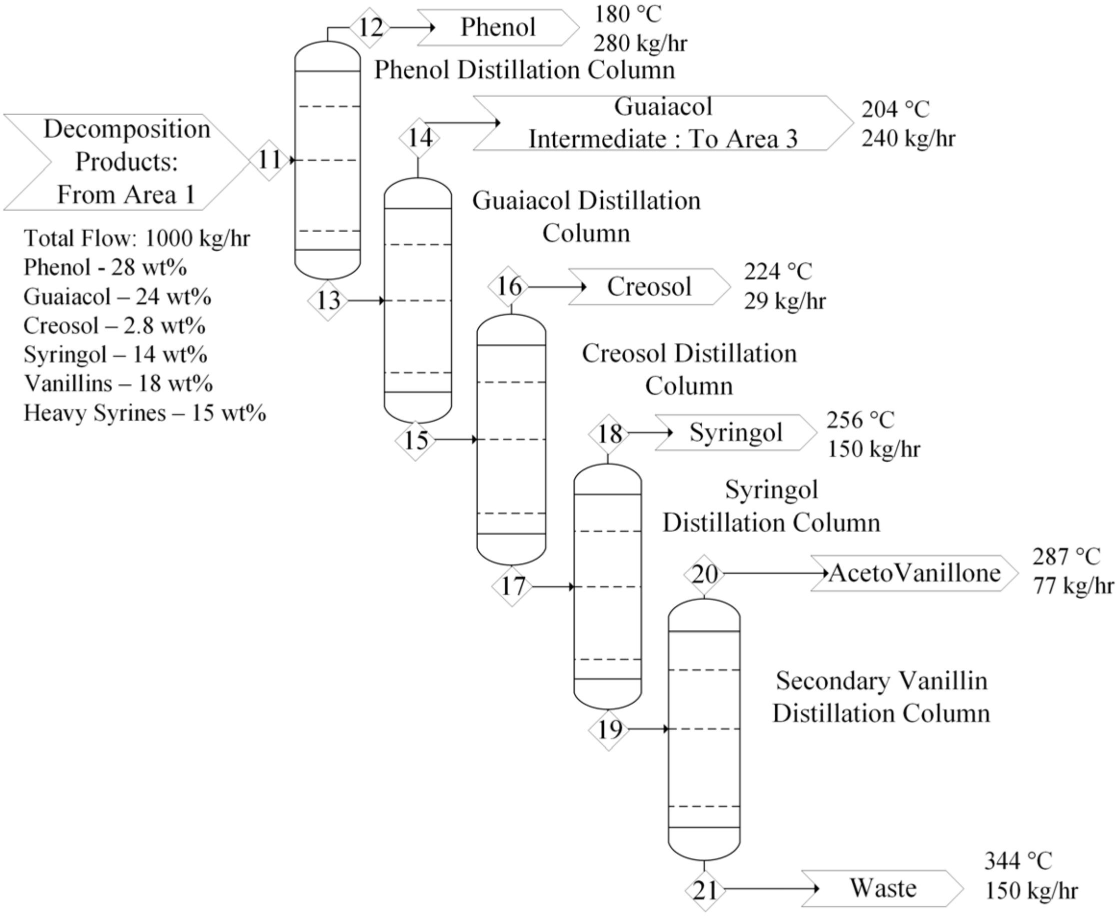

**Figure 2.** Simplified process area 2 (mass balance may not sum due to rounding).

charge of chemicals and catalyst is calculated based on the design ($440,000). Working capital is estimated as 10% of the fixed capital investment ($6.5 million). The total capital investment is the sum of the fixed capital investment, the initial charge of catalysts and chemicals, and the working capital. The total capital investment for the designed process was computed and approximated at $72 million ± $29 million.

### 3.3. Operating costs

The operating costs for the designed process are shown in Table 2. The operating costs are comprised of the raw material costs, chemical and catalyst costs, maintenance costs, lab charges, operating labor costs, and utility costs. The total operating cost per year for the designed process was calculated to be $39.8 million ± $16 million at a basis date of August, 2020. The operating cost increases slightly every four years when the catalyst needs to be fully replaced, resulting in a cost of $40.3 million ± $16 million for those years. The raw material, chemical and catalyst, and utility costs were determined using an operating factor of 95%.

Raw materials for the process consist of lignin and glyoxylic acid. The price for lignin was obtained from an NREL paper [36] for consistency with previous work and a spot price was used for glyoxic acid due to the unavailability of historical price data. Glyoxylic acid's price has risen greatly due to the effects of COVID-19. In order to mitigate COVID-19's effect on pricing, 60% of the spot price was used [37]. Overall, the total cost for raw materials is $10 million ± $4.1 million per year.

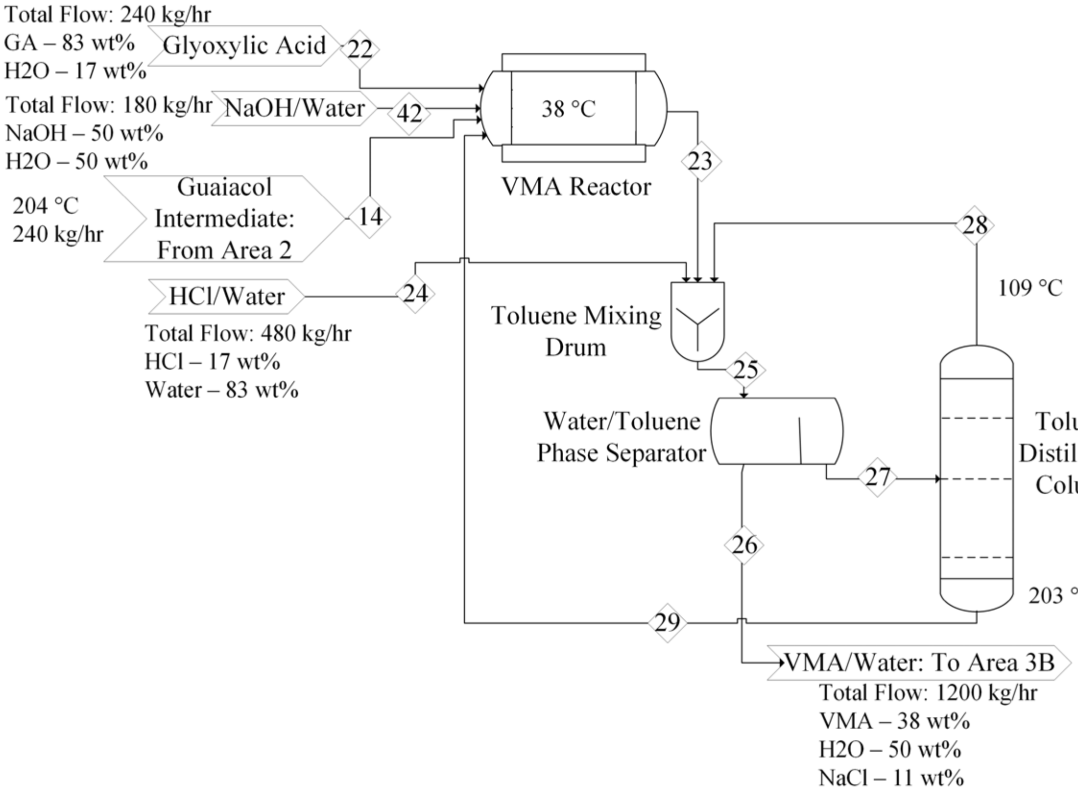

**Figure 3.** Simplified process area 3a. VMA = vanillylmandelic acid, EA = ethyl acetate (mass balance may not sum due to rounding).

The utility costs for the process consist of electricity, high-pressure steam, boiler feed water, and cooling water costs. The cost for each of the utilities was estimated using an in-house methodology except for electricity for which South Dakota electricity pricing was used [38]. The annual cost for utilities was calculated to be \$15.6 million ± \$6.2 million per year.

Maintenance costs were approximated as 4% of the total fixed capital investment (FCI). The total yearly cost for maintenance was calculated to be \$2.6 ± \$1.0 million per year.

The consumable chemicals required for the designed process are ethyl acetate, toluene, NaOH, process water, and HCl. The air used in the facility will be ambient air in order to operate direct fired heaters. One solid catalyst is necessary to facilitate the decarboxylation reaction to turn VMA into vanillin: Cu(II) oxide. The yearly catalyst replacement was assumed to be 5% of the total catalyst loading. The overall cost of chemicals and catalysts was calculated to be \$300,000 ± \$120,000 per year when the catalyst needs to be completely replaced and \$23,000 ± \$8,800 per year when it does not need to be replaced.

The operating labor cost was calculated assuming 4.5 8-hour shifts for round-the-clock staffing. It was computed that 6 outside operators per shift would be required based on the number of unit operations located within the process. Based on these values, a total of 32 operators are required. The average salary for the outside operators was found to be \$59,000 [39] for the state of South Dakota. This number was multiplied by 1.3 to include fringe benefits. One board operator per shift is also required to operate the designed process. The board operator salary was approximated as 120% of the fully loaded outside operator salary. Finally, operating supervision was estimated as 15% of the combined outside and board operators' salary. The total operating

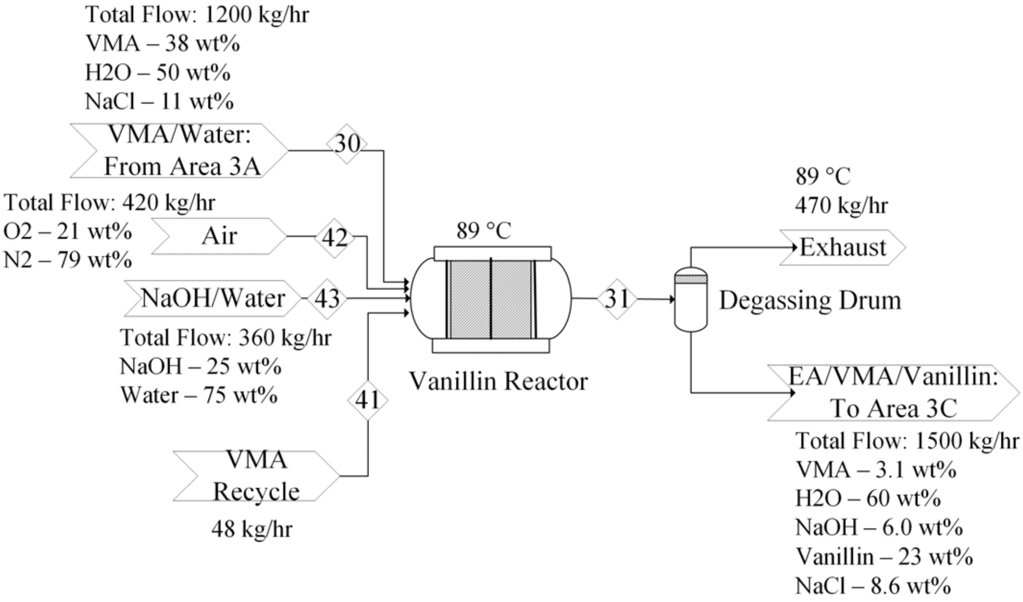

**Figure 4.** Simplified process area 3b. VMA = vanillylmandelic acid, EA = ethyl acetate (mass balance may not sum due to rounding).

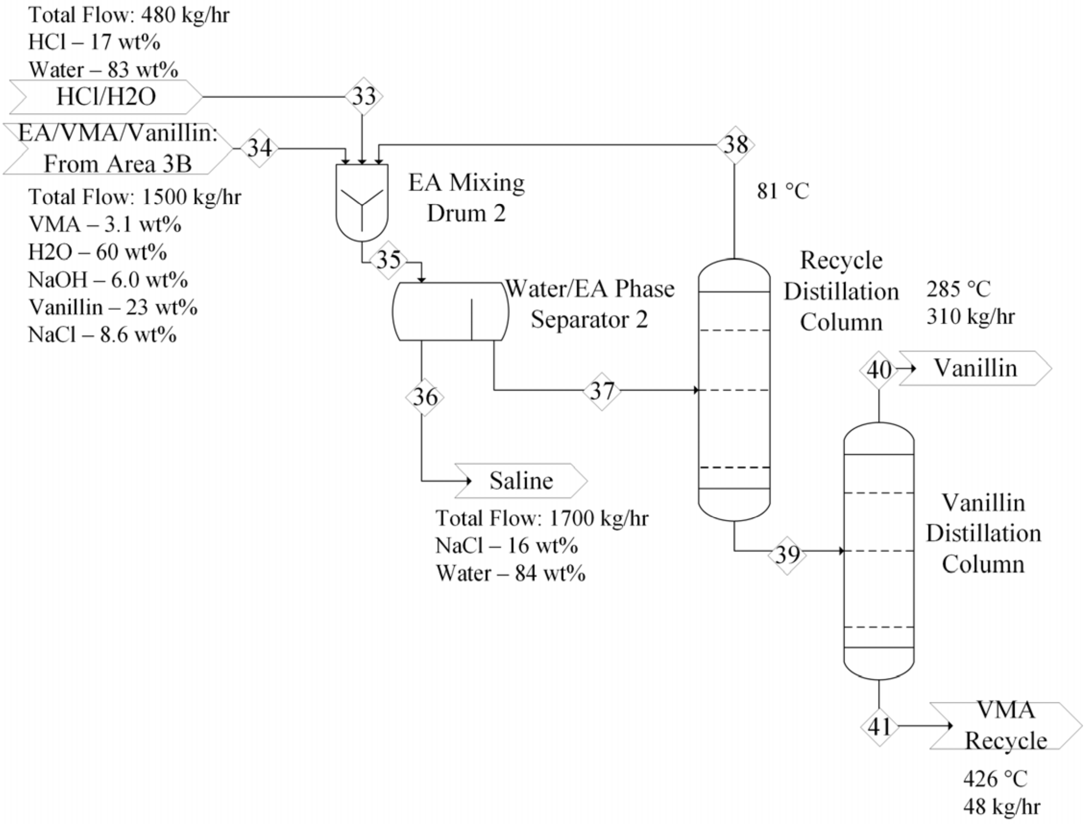

**Figure 5.** Simplified process area 3c. VMA = vanillylmandelic acid, EA = ethyl acetate (mass balance may not sum due to rounding).

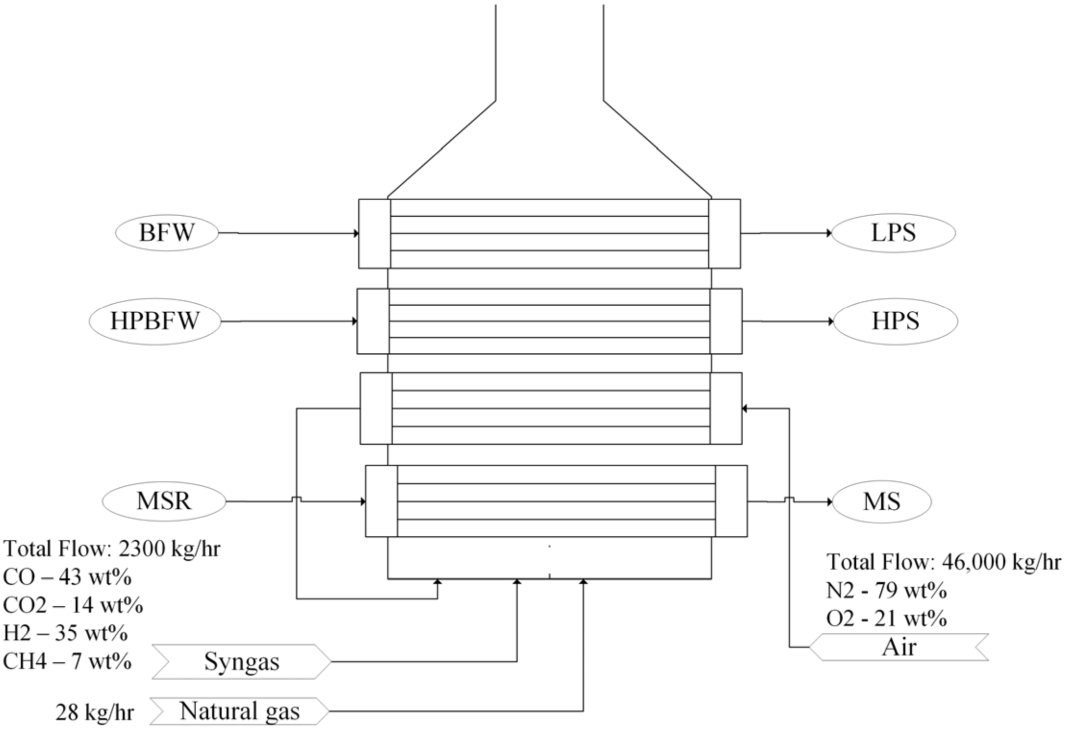

**Figure 6.** Simplified process area 4. BFW = boiler feed water, HPBFW = high pressure boiler feed water, MSR = molten salt return, LPS = low pressure steam, HPS = high pressure steam, MS = molten salt.

labor cost was computed to be \$3.1 million ± \$1.2 million per year.

While the process does generate three different types of waste and emissions, only the heavy syringol compounds produced at 150 kg/hr need to be treated and cannot be directly released. The cost of waste treatment was estimated at \$0.04/1000 kg of waste, resulting in an estimated cost of \$60 ± \$24 per operating year.

## 3.4. Cash flow

### 3.4.1. Revenues

The revenue generated by the designed process comes from the production of vanillin, phenol, creosol, and syringol. Credit for the combustion of syngas used to produce steam is incorporated into the operating costs to supply steam and natural gas. The sales price for vanillin was found using research papers as historical data were unavailable [27]. A 15% premium was added to the sales price of the vanillin due to its status as a 'natural', renewable product. The sale price for acetovanillone was assumed to be 60% of the price of vanillin. The saleable price for phenol was found using historical data. Other products were estimated using spot prices as historical data could not be obtained [40, 41]. The annual production rate for each of the products was computed using an operating factor of 95%. Based on the aforementioned price data, the annual revenue generated is approximately \$68 million ± \$27 million at a basis date of August, 2020.

### 3.4.2. Taxes

The economics for the designed process were developed by assuming that the facility would be built in the state of South Dakota, US. The federal tax rate for the process was assumed to be 21% and South Dakota currently has a 0% corporate income tax rate. Taxes such as property tax or purchasing tax for raw materials and consumable chemicals were not taken into consideration. When calculating depreciation, the US MACRS method was used with a depreciation schedule of 17 years.

**Table 1.** Capital costs (basis date Aug. 2020).

| **Equipment type** | **Number of units** | **Total module cost ($'000)** |
|---|---|---|
| Pumps | 25 | 1,500 |
| Heat exchangers | 28 | 6,300 |
| Compressors | 4 | 3,300 |
| Reactors | 3 | 760 |
| Pressure vessels | 34 | 7,300 |
| Direct fired heaters | 1 | 20,000 |
| Motors | 4 | 7 |
| Storage vessels | 1 | 3 |
| Conveyors | 2 | 630 |
| Total line item costs | | 40,000 |
| Additional direct costs | 0.3*TMC | 12,000 |
| Total direct cost | AMC+TMC | 52,000 |
| Indirect costs | 0.25*TMC | 13,000 |
| Fixed capital investment | TDC+IMC | 65,000 |
| Working capital | 0.1*FCI | 6,500 |
| Initial charge of chemicals & catalyst | | 390 |
| Total capital investment | C&C+WC+FCI | 72,000 |

### 3.4.3. Overall profitability

The cumulative discounted cash flow diagram for the designed process can be seen in Figure 7. The FCI for the process was spread out over 24 months and the economic operating lifetime of the plant was assumed to be 20 years. Using a hurdle rate of 20%, the NPV@20% was calculated to be $51 million ± $20 million at a basis date of August 2020. The discounted cash flow rate of return (DCFROR) was calculated to be 35% and the discounted payback time is 3.7 years.

## 3.5. Hazard analysis

The two most influential variables when determining profitability are the sales price of vanillin and the fixed capital investment (FCI). The impact of these variables is shown in Figures 8 and 9. A FCI variation of ± 40% resulted in an NPV@20% high of $80 million and low of $23 million. Variation within the region of most probable uncertainty for the FCI remains completely within the positive NPV region, indicating that variation of the FCI poses only a minor risk of unprofitability for this project. Variation within the region of most probable uncertainty for vanillin is mostly (97% by area) within the positive NPV region, indicating that variation of the vanillin sale price poses only a slight risk of unprofitability for this project. In order for this process to have a positive NPV@20% the salable price of vanillin must be at least $11.50/kg. The vanillin variation was based on reported price data ($10-$35/kg) and resulted in an NPV@20% high of $270 million and low of -$17 million.

**Table 2.** Operating costs ($'000).

| Time (years) | Operating labor | Maintenance | Utilities | Chemicals and catalysts | Operating materials and lab charges | Other direct costs |
|---|---|---|---|---|---|---|
| Without replacing catalyst | 3,100 | 2,600 | 16,000 | 22 | 730 | 22 |
| Replacing catalyst | 3,100 | 2,600 | 16,000 | 300 | 730 | 22 |

Table 2 continued..

| Time (years) | Total manufacturing costs | Raw materials | Total direct operating costs | Indirect costs | Total operating costs |
|---|---|---|---|---|---|
| Without replacing catalyst | 22,000 | 7,600 | 30,000 | 7,700 | 37,000 |
| Replacing catalyst | 22,000 | 7,600 | 30,000 | 7,800 | 38,000 |

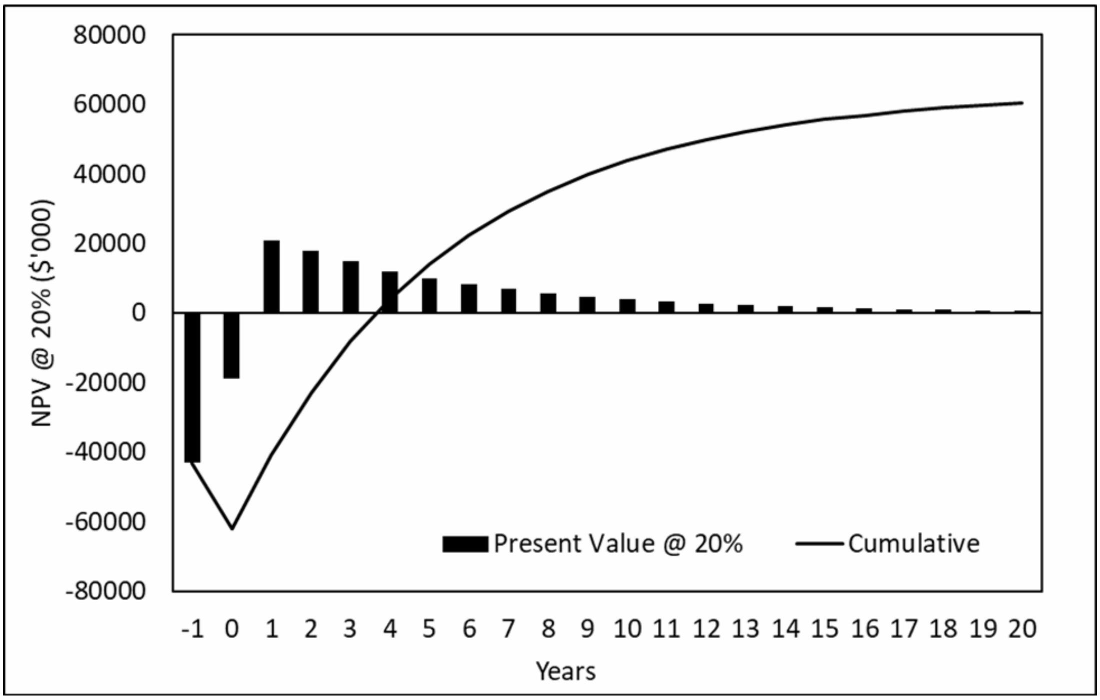

**Figure 7.** Cumulative discounted cash flow diagram of the process to produce vanillin and useful co-products from corn stover lignin.

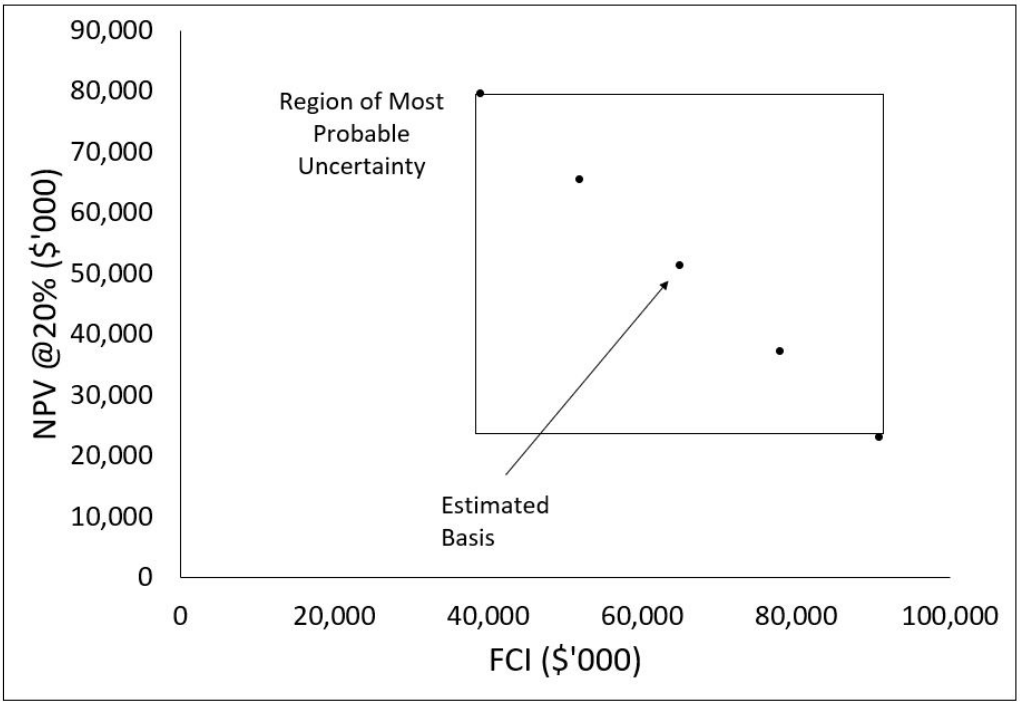

**Figure 8.** Economic hazard analysis of the fixed capital investment (FCI) estimate as measured using the net present value at a 20% hurdle rate (NPV@20%).

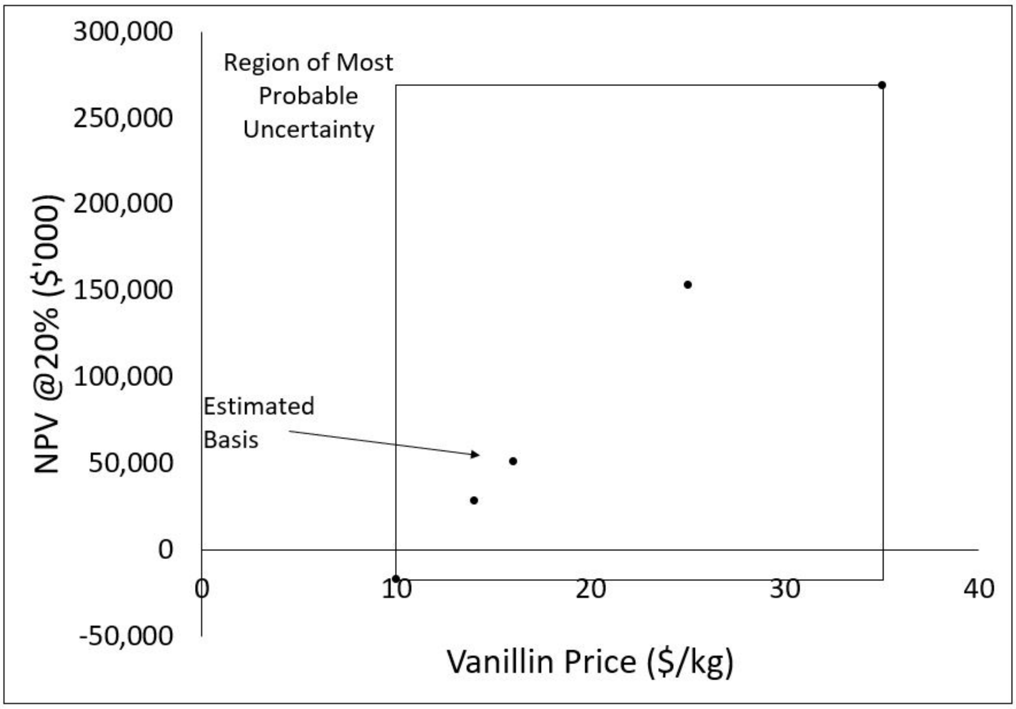

**Figure 9.** Economic hazard analysis of the vanillin sales price as measured using the net present value at a 20% hurdle rate (NPV@20%).

## 4. CONCLUSIONS

The majority of the revenue is produced from the sale of vanillin. In order to increase profits in addition to converting guaiacol to vanillin, phenol can also be converted to vanillin rather than sold as a co-product. The difference in sales price of \$15/kg suggests that this additional complexity may be worthwhile. While Figures 8 and 9 suggest that the project is expected to generate a profit with the most anticipated pricing estimates, the extent of that profitability is heavily tied to the price of vanillin. Therefore, it is recommended that the market outlook (supply and demand forecasts) and projected future pricing for vanillin be investigated heavily before moving forward with a project based on this design.

It may be possible to optimize the initial lignin decomposition reaction to produce more guaiacol. In addition, bench- or pilot-scale optimization of the extraction methods may be warranted to decrease costs.

In the current design unreacted lignin was assumed to be recyclable, and lab tests should be done to confirm this. In addition, the reaction gas phase amount and composition should be quantified.

Glyoxylic acid was assumed to not disproportionate under operating conditions and be recyclable. This should be confirmed through lab work. In addition, the extent of VMA and glyoxylic acid LLE separation should be quantified through lab work and optimized.

This process ignored the effects of dimers and oligomers. These compounds should also be considered to fully study the process.

The economic feasibility of vacuum columns that use steam as a heating fluid versus the use of higher pressure columns that requires molten salt as a heating fluid should be explored. In addition, more complicated or nontraditional distillation methods could be investigated.

Reactors R-302 and R-341 (VMA production reactor and vanillin production reactor, respectively) should be tested by lab work for the possibility of further optimization or alternate reactor setups, possibly even combining both reactors. Because the DCFROR is larger than the hurdle rate, this project is likely a worthwhile investment and should be investigated at a more in-depth level of design.

## ACKNOWLEDGMENTS

This research was funded by the North Dakota Corn Council.

## CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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