

2009

Techno-economic analysis of Di-butyl ketone, Di-methyl furan and Hydroxymethyl furfural production from biomass based resources

Akshay Dilip Patel
Iowa State University

Follow this and additional works at: <http://lib.dr.iastate.edu/etd>

 Part of the [Bioresource and Agricultural Engineering Commons](#)

Recommended Citation

Patel, Akshay Dilip, "Techno-economic analysis of Di-butyl ketone, Di-methyl furan and Hydroxymethyl furfural production from biomass based resources" (2009). *Graduate Theses and Dissertations*. 11024.
<http://lib.dr.iastate.edu/etd/11024>

This Thesis is brought to you for free and open access by the Graduate College at Iowa State University Digital Repository. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

**Techno-economic analysis of Di-butyl ketone, Di-methyl furan and
Hydroxymethyl furfural production from biomass based resources**

by

Akshay D. Patel

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Co-majors: Agricultural and Biosystems Engineering;
Biorenewable Resources and Technology

Program of Study Committee:
Robert P. Anex, Major Professor
D. Raj Raman
Brent Shanks

Iowa State University
Ames, Iowa
2009

Table of Contents

List of Figures	iv
List of Tables	v
Abbreviations	vi
Chapter 1: General Introduction	1
Chapter 2: Techno-economic analysis of 5-Nonanone (Di-butyl Ketone) production from Levulinic acid.....	5
Abstract	5
Introduction	6
Materials and Methods	7
Production Process	8
Economic model and key assumptions	10
Results and Discussion.....	12
Process analysis.....	12
Economic analysis.....	14
Sensitivity analysis.....	17
Bottlenecks and Approach	19
Conclusion.....	21
Acknowledgements	23
Abbreviations	23
References	23
Appendix 2.A Process Flow Diagram for Model ‘A’ (90% purity).....	26
Appendix 2.B Process Flow Diagram for Model ‘B’ (>99% purity).....	27
Appendix 2.C Description of Production Process and Economic Model	28
Process model.....	28
Section1: Feed Mixing and Reaction	28
Section2: Product Separation	31
Section3: DBK purification.....	32
Process economic model	33
Appendix 2.D Mass flows and Costs for key components.....	36
Model A:	36
Model B:.....	37
Cost of Chemicals:.....	38
Appendix 2.E List of Equipment and Cost estimates.....	39
Model A:	39
Model B:.....	39
Appendix 2.F Sensitivity parameters and values	41
Model A:	41
Model B:.....	42
Appendix 2.G Summaries of Process Engineering Analysis	43
Model A	43
Model B.....	44

Chapter 3: Techno-economic analysis of Dimethylfuran (DMF) and Hydroxymethylfurfural (HMF) production from pure fructose in catalytic processes.....	45
Abstract	45
Introduction	46
Materials and Methods	47
Process Description and Flow Diagram	50
HMF production process	50
DMF production process	51
Results and Discussion	53
HMF production	53
DMF production	56
Conclusion	62
Acknowledgements	63
Abbreviations	63
References	63
Appendix 3.A Equipment list and Cost estimates	65
Appendix 3.B Sensitivity parameters and values	68
Appendix 3.C Summary of Process Engineering Analysis	69
HMF Production	69
DMF Production	70
Chapter 4: General Conclusions	71
Future Work	75
Acknowledgements	76

List of Figures

Figure 2.1 Process block diagram for conversion of Levulinic acid to Dibutyl Ketone	8
Figure 2.2 Distribution of capital expenses	15
Figure 2.3 Distribution of operating expenses	16
Figure 2.4 Sensitivity analysis of change in MSP	18
Figure 2.5 Sensitivity analysis for change in MSP	18
Figure 2.6 Process Flow Diagram for Model A	26
Figure 2.7 Process Flow Diagram for Model B	27
Figure 3.1 HMF production process block diagram	51
Figure 3.2 DMF production process block diagram	52
Figure 3.3 Sensitivity analysis on minimum HMF selling price	55
Figure 3.4 Major contributors to DMF price	58
Figure 3.5 Sensitivity analysis on minimum DMF selling price	59

List of Tables

Table 2.1 Mass flow rates of key components.....	12
Table 2.2 Characteristics of product stream	14
Table 2.3 Capital Expenses.....	14
Table 2.4 Operating expenses.....	15
Table 2.5 Results of Discounted Cash flow analysis.....	16
Table 2.6 Fractional Conversion of Levulinic acid to products.....	30
Table 2.7 Mass Flow and properties of key streams for Model A.....	36
Table 2.8 Mass Flow and properties of key streams for Model B.....	37
Table 2.9 Cost of Chemicals.....	38
Table 2.10 Equipment list and Installed cost for Model A.....	39
Table 2.11 Equipment list and installed cost for Model B	39
Table 2.12 Sensitivity parameters and values.....	41
Table 3.1 Feed and product flow rates for HMF production process.....	53
Table 3.2 Installed equipment cost for HMF production.....	54
Table 3.3 Feed and product flow rates for DMF production	57
Table 3.4 Installed equipment and catalyst cost for DMF production.....	57
Table 3.5 Equipment list and installed equipment cost for DMF production.....	65
Table 3.6 Sensitivity parameters for DMF production	68

Abbreviations

LA – Levulinic acid

DBK – Dibutyl Ketone (5-Nonanone)

HMF – 5-Hydroxymethyl Furfural

DMF – 2,5-Dimethyl Furan

MEK – Methyl Ethyl Ketone

NaCl – Sodium Chloride

HCl – Hydrochloric acid

FDCA – 2,5-Furan di-carboxylic acid

MSP – Minimum Selling Price

CSTR – Continuously Stirred Tank Reactor

PFTR – Plug Flow Tubular Reactor

MT – Metric Tonnes

Gal – Gallons

MM\$ – Million US Dollars

MMGal – Million gallons

Chapter 1: General Introduction

Energy and chemicals based on carbon play a pivotal role in our lives. The growth of our economy depends on the sustained availability of energy and chemicals. Over the past century, petroleum has provided us with a cheap and readily available source of carbon to meet our needs. However the rate of petroleum usage makes it a finite and unsustainable source for energy and chemicals. The significant proportion of petroleum in the energy supply mix also has implications in the areas of national security with a handful of countries controlling most of the world's supply. The increased reliance on petroleum also leaves us economically vulnerable due to increased debt and exposure to volatile price movements associated with petroleum. In contrast biomass derived carbon enables a sustainable system which recycles carbon at a rate commensurate with its usage. It is environmentally friendly in the long run and more importantly is a renewable and domestic resource, thus addressing some of the major issues surrounding petroleum. Many pathways are being developed to convert biomass into hydrocarbon compounds to meet our energy and chemical needs. The major challenge with utilization of biomass is its high oxygen content. The chemical industry today has mainly evolved around low oxygen chemical compounds. Significant progress has been made in transforming these chemical compounds to useful products. Hence, it is essential to efficiently remove oxygen from biomass to economically produce chemical compounds thus utilizing the current infrastructure to the maximum possible extent.

Biomass can be converted to chemicals through two main pathways. One is the biochemical route which involves use of genetically engineered microorganisms to convert biomass or high oxygen compounds derived from biomass to useful chemical compounds. With the rapidly evolving knowledge of genetics, new microorganisms can be potentially engineered to selectively produce a highly specific product, with high conversion efficiency and concentrated product streams. This can lead to the production of high purity compounds which may require minimal separation. However reactions using microorganisms can take significantly longer production time due to the time required for growth of organism and also the inability to use high temperature and pressure to thermodynamically drive the reaction in

desired direction. The other is the chemical pathway which involves use of homogenous or heterogeneous catalysts in conjunction with heat and pressure for conversion of biomass. The catalysts are engineered using a mix of inorganic and organic elements. Conversion using chemical catalysts can be less selective and less efficient as compared to potential microorganisms. Also complex separation problems can be expected due to a mixture of compounds in the product stream. However the use of chemical catalysts enables the application of high temperature and pressure to favorably drive the reaction thus leading to product formation in a fraction of the time required through the biochemical route. Both these pathways have their own benefits and drawbacks. It is essential to analyze the feasibility of these pathways in a given scenario. The economics of the biochemical pathway has been studied to some extent and has led to the implementation of biochemical based conversion processes on large scale, for example in case of polylactic acid production. The economics of the chemical route for production of chemicals from biobased compounds have not been studied so far. Many promising new processes have been developed which enable conversion of biomass to useful chemicals using chemical catalysts. Techno-economic analysis will help us analyze the feasibility and identify challenges for implementation of these processes. It provides information about possible large scale production yields, the capital costs for implementation, operating costs and product price. Sensitivity analysis helps us quantify the impacts of critical parameters on yields, costs and price.

This thesis reports the analysis of two representative processes based on chemical conversion. These processes were developed by Dr. Dumesic and his group at University of Wisconsin. We are thankful to them for providing data for this analysis. The analysis has been done by using process and economic models which simulate large scale implementation of the processes. Both processes are based on chemical conversion of biobased starting materials and lead to the production of sustainable industrial chemical compounds with wide ranging applications. The processes represent the use of levulinic acid and fructose as starting materials from biomass and lead to ketone and furan compounds which have applications as industrial solvents and starting materials for paints, resins, and pharmaceutical products. They also illustrate the synergies that can be achieved in a biorefinery wherein by-product

from one process is used as a feedstock for other. Both the processes studied involve use of different strategies for removal of oxygen. The Thesis has been presented in the Journal article format, and includes the analysis in the form of two articles which are yet to be published.

The first process presented in Chapter 2 uses levulinic acid as a feedstock. It represents the use of platform chemicals from biomass for production of industrial chemicals. Levulinic acid can be obtained from dehydration of biomass using homogeneous chemical catalysts. The analyzed process involves hydrogenation and condensation of levulinic acid over two catalyst beds in a single reactor to produce Dibutyl Ketone (DBK) along with other useful by-products which include 2-heptanone, 3-hexanone, nonane, butane and pentanoic acid. This process removes one half of the oxygen in levulinic acid as water by addition of external hydrogen and one third of the oxygen as carbon dioxide. The products formed are separated to produce pure DBK. Ketones form an important class of commercially useful chemical compounds. Dibutyl Ketone has applications as an industrial solvent for use in chemical manufacture and paints. It potentially can be converted to nonane for use in fuel applications. It can also be used as a chemical intermediate in production of a variety of other compounds. This study presented in the first paper was conceived by Dr. Robert Anex who has reviewed and edited the manuscript and has been involved in the analysis for this study. A. Patel performed the techno-economic modeling and analysis on which this study is based and prepared the manuscript. Dr. Juan Carlos provided the process data for this analysis and has reviewed and edited the manuscript. Dr. James Dumesic has provided guidance in development of the process analyzed in this study.

The second process presented in Chapter 3 utilizes fructose sugars as feedstock. Fructose can be produced from biomass through either biochemical or chemical routes. This process represents the use of sugars as a feedstock for the production of compounds with industrial chemical and fuel applications. The process involves dehydration of fructose using a homogeneous catalyst in a biphasic tank reactor to produce 5-hydroxymethyl furfural (HMF) and levulinic acid as a byproduct. The HMF produced has potential applications for

use as a chemical intermediate to produce furfural and furan derivatives which can be used in production of resins, polymers, solvents and pharmaceuticals. HMF can be converted to 2,5-furandicarboxylic acid which can be a potential replacement for terephthalic acid in polymer production. Here we consider a process in which HMF is converted to 2,5-Dimethyl Furan (DMF) by hydrogenolysis over a copper ruthenium catalyst. This process uses external hydrogen to remove oxygen from the starting compound. DMF can potentially be a gasoline substitute and it can also have applications as solvent and chemical intermediate for other important furan based compounds. This study was conceived by Dr. Robert Anex who has reviewed and edited the manuscript and has been involved in the analysis. Dr. Feroz Kabir developed the process model used in this study and prepared the first draft of the manuscript. The economic modeling and analysis for this study was performed by A. Patel who also contributed to writing and editing the manuscript. Dr. Juan Carlos reviewed the manuscript. Dr. James Dumesic and his group developed the conversion process and have provided laboratory-scale process data used in this analysis.

Chapter 2: Techno-economic analysis of 5-Nonanone (Di-butyl Ketone) production from Levulinic acid

A paper to be submitted to the Journal of Biofuels, Bioproducts and Biorefining

Akshay Patel¹, Juan Carlos Serrano-Ruiz², James A. Dumesic², Robert P. Anex¹

¹Department of Agricultural and Biosystems Engineering, Iowa State University,
Ames, IA 50011

²Department of Chemical and Biological Engineering, University of Wisconsin, 1413
Engineering Drive, Madison, WI 53706

Abstract

The issues associated with the use of petroleum have led to the development of new processes for the production of industrial chemicals from biomass resources. Thus, a sustainable supply of industrial chemicals can be made available through use of biobased sources. Techno-economic assessment of such processes in conjunction with lab scale development is essential to analyze feasibility and identify key areas for further development. We analyze here a process for production of 5-nonanone (dibutyl ketone, DBK) from levulinic acid (LA) which is a biobased platform chemical that is produced in large quantities from a variety of lignocellulosic biomass sources. The economic analysis herein described is based on a catalytic pathway developed in lab scale. The final product (DBK) has applications as an industrial solvent and serves as a platform chemical for the production of liquid hydrocarbon fuels in the diesel and gasoline ranges. A detailed process model has been created using Aspen for two different product purity levels (90 and 99 %). Process economics have been studied in a discounted cash flow analysis to analyze the viability of production and relative product purification costs. Sensitivity analysis is used to identify the impact of key parameters on the minimum selling price of product. The modeled process utilizes 480 MT/day of LA feedstock to produce 194 MT/day of 5-nonanone along with other byproducts. Two models, involving the production of 5-nonanone at two different purity

levels, allow us to compare the costs and benefits of using 5-nonanone as chemical (high purity) and as a platform molecule for fuel production (lower purity).

Keywords: Biobased Chemicals, 5-Nonanone, Levulinic acid, Techno-economic analysis.

Introduction

A majority of the industrial chemicals used currently are derived from petroleum based resources. Industrial chemicals facilitate or lead to the production of a wide variety of products and thus are an essential and integral part of our economic activities. With the insecurity surrounding continued availability (1) and environmental effects of petroleum resources, it is essential to look towards alternative biorenewable sources for these chemicals (2). Biorenewable sources offer a variety of benefits over use of petroleum feedstocks. However, it is essential to analyze the technical and economic feasibility of biobased processes in order to substitute current petrochemical-based technologies by those derived from renewable biomass. A large variety of new chemicals are being developed on lab scale using platform chemicals such as glucose (3), levulinic acid (4, 5), and hydroxyl-methyl furfural (6) which can potentially be derived on large scale from a range of biomass resources. In this sense, it is important to analyze the viability of these processes at an early stage in the development so critical bottlenecks and areas for further development can be identified before this technology is scaled up.

The analysis herein described involves a process to produce 5-nonanone from concentrated aqueous solutions of LA. LA is a platform chemical which can be obtained from a wide range of cellulosic biomass feedstocks including wastes (5, 7). Large scale production of LA from biomass can be possible through a currently well-established patented technology (8). By means of this process, LA can be produced at very low price (\$0.04-\$0.10 per pound), thus enabling its use as platform molecule for the production of other important chemicals such as methyl-tetrahydrofuran (MTHF, an important fuel additive), δ -aminolevulinic acid (DALA, a biodegradable insecticide) (5) and, in the case of the present paper, DBK. DBK is an important industrial solvent with applications in paints, resins and a

variety of other areas (9). Additionally, DBK can also potentially serve as platform molecule for the production of liquid hydrocarbon fuels for the transportation sector (10).

The process herein described involves the catalytic processing of LA to DBK in two steps which are carried out in a single reactor with two catalytic beds in a cascade arrangement. As a part of this analysis, we have carried out the simulation of this route and the subsequent purification steps in an engineering process and economic model, which is then used to analyze various aspects of this technology. The process has been modeled to utilize 480 MT/day of LA which is based on the assumption of a 2000MT/day biomass refinery facility producing LA (8). It leads to the production of DBK along with a mixture of hexanone, heptanone, n-nonane, n-butane and pentanoic acid as by-products. The high scale approach allowed us to evaluate possible fuel and chemical applications for DBK. With the exception of pentanoic acid, the rest of by-products and gases are relatively easily separated from the product stream, while the separation of pentanoic acid requires significant further processing. Hence, two scenarios have been modeled, one with 90% product purity (suitable for fuel production) and other with >99% product purity (chemical grade) to evaluate the costs and benefits involved in further purifying the product for its use as chemical.

Materials and Methods

The modeled process uses 480 MT/day LA which undergoes catalytic processing to yield DBK along with other by-products. The models are steady state process simulations. The actual lab scale data (reaction conditions, product composition, yields, catalyst, and reactor information) were provided by the Dumesic's research group at the University of Wisconsin-Madison. The production and purification process was modeled using ASPEN Plus process engineering software which enabled a process flow diagram and mass and energy balances. Two models were created; the first one involves processing in reactor and less rigorous purification resulting in 90% pure DBK (pentanoic acid being the major impurity). The second model involves further purification leading to a product with >99% purity. The models are referred to as model 'A' (90% purity) and model 'B' (>99% purity) throughout the analysis. Laboratory data was used to size the reactor while data from the Aspen model was used to size rest of the process equipment. The stream results from Aspen

were imported into MS Excel (11) which was used to create an engineering economic model. A discounted cash flow analysis at a set internal rate of return was carried out to arrive at a Minimum Selling Price (MSP) for DBK with a net present project value of zero. This analysis has been carried out with 2007 dollar value as a point of reference. The models have been constructed to update all the cost values accordingly based on relevant indices. The two process models are at the same scale and differ mainly in the presence of additional purification processes on the front end of the reaction and initial separation steps. Figure 2.1 shows the process flow diagram. The sections '1' and '2' are common to both the models, while the section '3' involves further purification process to produce pure DBK and is present only in model 'B'. Detailed process flow diagrams and description of the process can be found in Appendix 2A and 2C respectively.

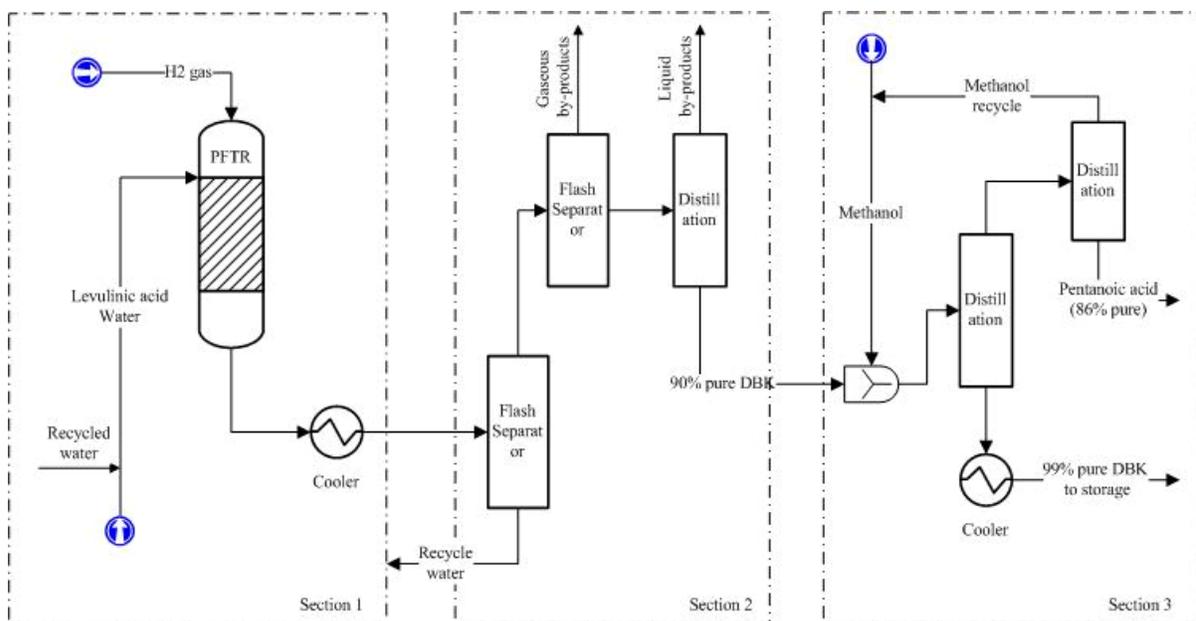


Figure 2.1 Process block diagram for conversion of Levulinic acid to Dibutyl Ketone

Production Process

The section 1 (Figure 2.1) involves feed mixing and reaction. LA and hydrogen gas are the major raw materials required for the process. A 50 wt% solution of LA in water is fed to the reactor along with hydrogen gas. In a plug flow tubular reactor LA reacts to yield DBK, CO₂ and water, as indicated in reaction 1:



The catalyst beds are operated at 350°C, 34 atm, pressure and a weight hourly space velocity (WHSV, defined as mass of LA fed per hour/ mass of catalyst used) of 1 h⁻¹. 100% of the LA fed is converted in the reactor. The overall reaction produces DBK as the main product, with 2-heptanone, 3-hexanone, n-nonane, n-butane and pentanoic acid being the by-products of the process. Water, unreacted hydrogen and carbon dioxide are present in the reactor output along with the product and by-products.

In section 2 (Figure 2.1), the reactor output stream is cooled and flashed to separate out water which is recycled after purging. The remaining stream is flashed again at a lower temperature and pressure to separate the gaseous by-products which mainly include carbon dioxide, unreacted hydrogen and butane gas. The liquid output from the second flash is subjected to distillation to separate out remaining by-products. The liquid distillate, which forms the liquid by-product stream, consists of a mixture of 2-heptanone, 3-hexanone, n-butane, n-nonane and small amounts of pentanoic acid. The liquid obtained downstream includes DBK with 90% purity, with pentanoic acid (9.2%) and other components present in trace quantities accounting for the rest of products. In case of model 'A', the bottoms product is the final product stream which is cooled and sent to storage. Alternatively, the liquid obtained from section 2 can be further purified in section 3 (model B). The overlapped boiling points of DBK and pentanoic acid prevented the utilization of distillation techniques for DBK purification. Instead, and after simulations with a wide range of polar solvents, and extraction with methanol was chosen to aid the separation process. Methanol is then mixed with the impure DBK stream from section 2, and the resulting stream is passed through a series of distillation columns which are sequenced so that the bottoms product from each is 99% pure DBK and the distillate is fed to the following column. This strategy allows the recovery of 98% of the methanol from the pentanoic acid by-product at the end of separation sequence, and 4% is purged out before recycle. As a result, pentanoic acid can be obtained with 87% purity as byproduct while the pure DBK streams are mixed and cooled before being sent to storage.

Economic model and key assumptions

A discounted cash flow analysis is used to assess the process economics which are modeled using an Excel spreadsheet following NREL model (11). The stream data for material, heat and work streams is imported into the spreadsheet from Aspen model. The process equipment was sized using standard procedures (12) which are described in Appendix 2C. The purchased equipment cost (PEC) was estimated using data from PT (12), NREL Ethanol design report 2001 (11) and ICARUS process evaluator. Total installed equipment cost (TIC) and indirect plant expenses have been set as fractions of purchased equipment cost. Installation costs include charges for equipment installation, instrumentation, piping, electrical connections, building, warehouse and site development. Indirect expenses include costs for engineering and supervision, construction expenses, legal and contractor fees. Contingency cost is estimated as 20% of the total direct and indirect plant costs. The total direct and indirect costs along with the contingency give an estimate of the fixed capital investment (FCI) required for the project. Working capital accounts for the startup costs and is estimated as 15% of FCI. The FCI and working capital constitute the total capital investment (TCI) in the project. The prices for feedstock, raw materials and by-products have been derived from market data and conservative estimates based on assumptions. It is assumed that utilities required for the plant are purchased and the wastewater treatment is carried out for a fixed price at an external facility. Labor costs are estimated based on general assumptions for employee hours required per day for the number of operating steps. Overhead expenses are accounted as a fraction of labor costs and maintenance costs are calculated as a fraction of the total purchased equipment cost. Insurance and legal fees are calculated as a fraction of installed equipment costs. These comprise the operating costs for the process. The cost of catalyst is incurred at every 10 year intervals in the discounted cash flow analysis. Currently it is priced at \$4000 per kg. In the absence of exact information about the catalyst composition, a long lifetime is assumed to factor in the possible recycle of catalyst materials, which can substantially reduce the recurring cost of catalyst.

The discounted cash flow analysis is based on certain assumptions and takes into account cash flows over the entire plant life. In the current analysis the selling price of DBK

is iterated at a set internal rate of return to gain a net project value of zero. This price at zero net present value is the Minimum DBK Selling Price (MSP). The following are some of the major assumptions critical to the analysis.

- The process has been modeled to utilize 480 MT/day of LA which is assumed to be produced from processing 2000MT/day cellulosic biomass through the Biofine process (13).
- Full set of reaction kinetics are unknown and hence experimental yields are used in analysis. The reactor size is estimated using residence time and catalyst bulk density.
- Plant operates on a continuous basis for 8400 hours every year.
- This analysis assumes an nth plant being built. The risk of unforeseen expenses incurred in setting up of a pioneer plant based on new process technology, has not been included in this analysis
- The LA feedstock price is assumed to be \$3.21 per kg (14). However, based on Biofine technology, substantial lower prices for levulinic acid are possible, and this possibility will be taken into account.
- The plant is 100% equity financed and the lifetime is assumed to be 20 years.
- Catalyst has a salvage value at the end of lifetime, which is recovered.
- All the costs and prices are updated to 2007 dollar value using appropriate indices.

Results and Discussion

Process analysis

The steady state flow rates of raw materials, product and byproducts streams are summarized in Table 2.1 (detailed flow diagrams for both processes, key stream results and costs of chemicals, as well as the summary of the results from process engineering model are included in Appendices). Both simulated processes described above use a 480 MT/day stream of pure LA as feedstock, resulting in production of 215 MT/day of 90 % purity DBK (model A) and 194 MT/day of high purity DBK (model B). As a result of the LA processing, a liquid by-products stream of 55 MT/day is produced, mostly composed of n-nonane (with application as diesel blender agent) and ketones in the C₆-C₇ range (Table 2.1).

Table 2.1 Mass flow rates of key components

	Model A(90% purity)(MT/day)	Model B(>99% purity)(MT/day)
Raw Materials		
Levulinic acid	480	480
Water	156	33
Hydrogen gas	41.6	41.6
Methanol	-	1.5
DBK production	215	194
DBK	195	193
Impurities	20(Pentanoic acid)	1
Liquid by-product stream	55	55
3-Hexanone	27	27
2-Heptanone	10	10
Nonane	11	11
Butane	4	4
Pentanoic acid	1.3	1.3
	Contd.	Contd.

	Model A(90% purity)(MT/day)	Model B(>99% purity)(MT/day)
Gaseous by-products	173	173
Hydrogen	25	25
Carbon di-oxide	136	136
Butane	11	11
Pentanoic acid stream	-	22
Pentanoic acid	-	19
DBK	-	2

The gaseous by-products include about 15% unreacted hydrogen, 79% carbon dioxide and 6% butane. Even though in this analysis this stream is treated as a by-product with low value, an attempt can be made to separate out hydrogen and butane from the mixture, allowing the recycle of the unreacted H₂ to the main reactor and the use of butane for the generation of heat required for the process. The CO₂-enriched stream obtained after the separation unit could then be potentially used in applications like algae growth for the purpose of lipids production (19). Alternatively, the gaseous by-product stream could be used, without the need of separation, for the production of methanol (necessary for the extraction strategy of section 3, Figure 2.1) by means of catalytic hydrogenation of CO₂ (20) using the remnant hydrogen from the DBK processing. All these improvements in the process can result in a more favorable economic analysis. In case of model 'B' an extra purification step is used to purify DBK leading to the production of a 22MT/day stream of pentanoic acid with 86% purity. This product can be further purified for applications in a wide variety of areas including lubricants, plasticizers, and pharmaceuticals (15).

The characteristics of the product stream for both the process models are given below.

Table 2.2 Characteristics of product stream

Product stream	Model A(90% purity)	Model B(>99% purity)
Mass flow rate(kg/hr)	8983	8100
Volumetric flow rate(m ³ /hr)	10.9	9.9
Temperature (°C)	30	30
Pressure(kPa)	101.3	101.3
Density(kg/m ³)	821	814
State	Liquid	Liquid

Economic analysis

The capital expenses for the production of DBK from LA are summarized in Table 2.3 (a more detailed list of capital expenses for each processing unit can be found in Appendix 2E). Section 1 accounts for a large fraction of the total installed costs, with reactor representing the major expense in this sense (75 % of total installed cost for model A and 57 % of total installed cost for model B). As expected, Model ‘B’ requires an excess of \$6.4M in Total Capital Investment mainly due to the increased capital requirements for additional purification section.

Table 2.3 Capital Expenses

	Model A(90% purity)(MM\$)	Model B(>99% purity)(MM\$)
Process section		
1. Feed Mixing and reaction	10.3	10.8
2. Initial separation	2.5	2.2
3. Purification	-	3.2
Total installed equipment cost	12.8	16.2
Total direct and indirect costs	18.3	23
Contingency	3.7	4.6
Fixed capital investment	22	27.6
Working capital	3.3	4.1
Total capital investment	25.3	31.7
Lang factor	4.6	4.6

The chart below depicts the fractions of each section, with reactor cost excluded from the feed mixing and reaction section.

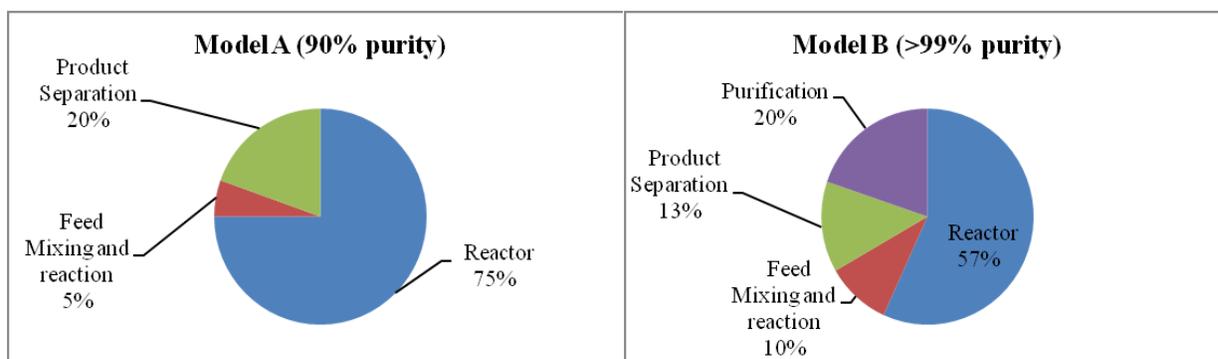


Figure 2.2 Distribution of capital expenses

The operating expenses are included in Table 2.4. As is evident from the numbers, the cost of the feed LA is a major contributor to the operating expenses that accounts for 97% of the total operating costs. As will be discussed below, the price of LA is a crucial factor determining the economic feasibility of the process. The utility costs are higher in case of Model B due to additional requirement in the purification area. However, a higher by-product credit is obtained in this case due to the separation of pentanoic acid, which can be sold separately at a higher price than the mixed by-product stream.

Table 2.4 Operating expenses

Operating expenses	Model A (MM\$/year)	Model B (MM\$/year)
LA Feed	539.28	539.28
Utility costs	10.02	10.48
Labor costs	2.05	3.41
Overhead and maintenance(O&M)	1.23	2.05
Others	2.45	2.89
Total expenses before credit	598.24	626.73
By-product credit	12.63	20.25
Net total expenses	542.40	537.86

The charts below indicate the distribution of operating expenses.

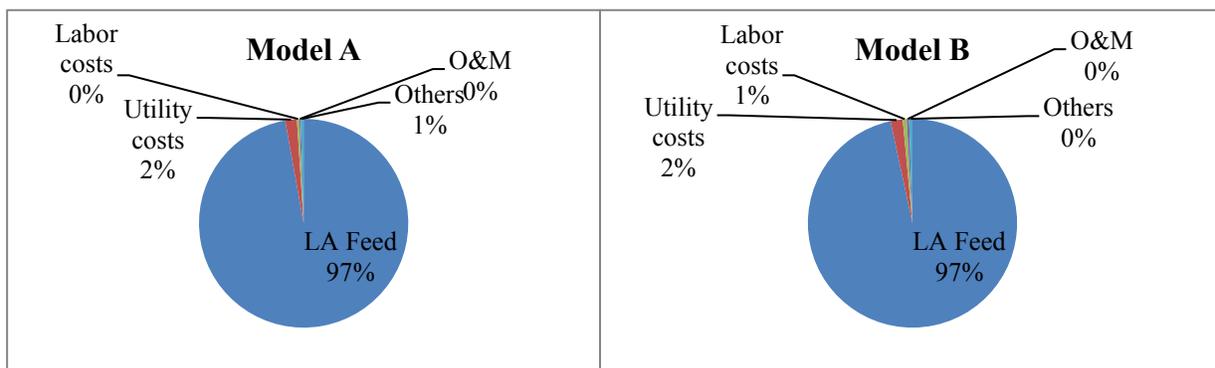


Figure 2.3 Distribution of operating expenses

Table 2.5 shows the final results from the discounted cash flow analysis, including the MSP for DBK for both models.

Table 2.5 Results of Discounted Cash flow analysis

	Model A	Model B
Annual LA input(MT/year)	168,000	168,000
Annual DBK production(MT/year)	75,452	68,035
Product yield (kg/MT feed)	450	405
Total Capital Investment(MM\$)	25.3	31.7
Catalyst cost (MM\$)*	197.7	197.7
Minimum Product Selling price(\$/kg)	7.70	8.49
Minimum Product Selling price(\$/gal)	24.05	26.18

*Discounted value

The higher DBK production and yield in model A is mainly due to the presence of impurity in product stream since the loss of DBK product in purification is minimal. For model B, an LA input of 168,000 MT/year produces 68,035 MT/year of high purity DBK. This is a reasonable scale for solvent applications, when compared with Methyl Ethyl Ketone (MEK) which is expected to have a worldwide market demand of 1.3 MMT by 2010 (16). The product yield is 405 kg/MT of LA which is obtained for a 98% of the experimental yields and about 66% of the stoichiometric yields. This shows that the losses in purification

process are minimal. The total capital investment is estimated to be 31.7 MM\$ and is comparable to MEK production from isobutene which is estimated to require an investment of about 34MM\$ for a similar capacity. The present value of catalyst cost at 198 MM\$ over the entire plant life is significantly higher as compared to the total capital investment in the project. About 40 MT of catalyst priced at \$4000 per kg is needed to maintain continuous production at the modeled scale. Thus, research for new inexpensive materials as catalysts seems to be important in order to ensure economic feasibility of the process.

The MSP for DBK is higher (by 15%) in case of model B since a higher purity product is obtained and can justify its price. Importantly, the cost of LA feed is the major factor influencing MSP and the overall project feasibility. The MSP for a high purity DBK was found to be \$8.49 per kg, which is comparable to the current DBK purchase price (\$9.07 per kg) (17). However, for large scale solvent applications similar to MEK, the price is quite high when compared to MEK price of \$0.77 per kg (18).

Sensitivity analysis

Process and economic sensitivity analysis has been performed to gauge the impact of variations in key parameters on the MSP and results are shown in Figure 2.4 and 2.5 for Model B. The values for these parameters are based on experimental data or assumptions. Based on our confidence in the assumed values, we have studied the effect of 20% variation in these parameters on the MSP of DBK. This analysis helps in identification of key bottlenecks and provides a direction for future development in this process. As can be seen, the feedstock price and the DBK yield are, by far, the two parameters most affecting the MSP, with the catalyst price and the credit obtained from byproducts having much less impact on the economics of the process.

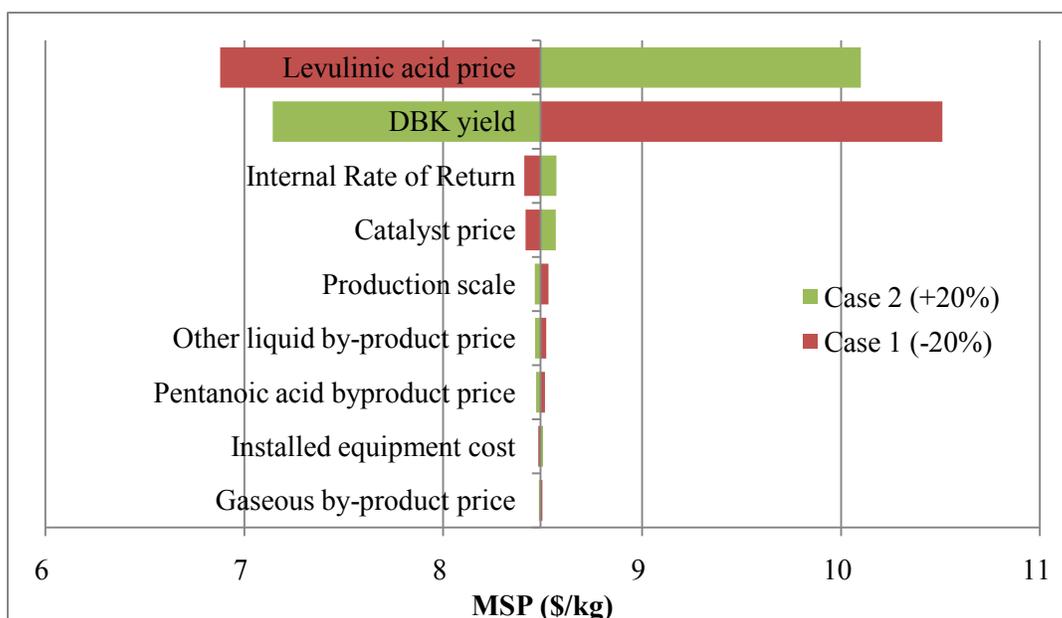


Figure 2.4 Sensitivity analysis of change in MSP

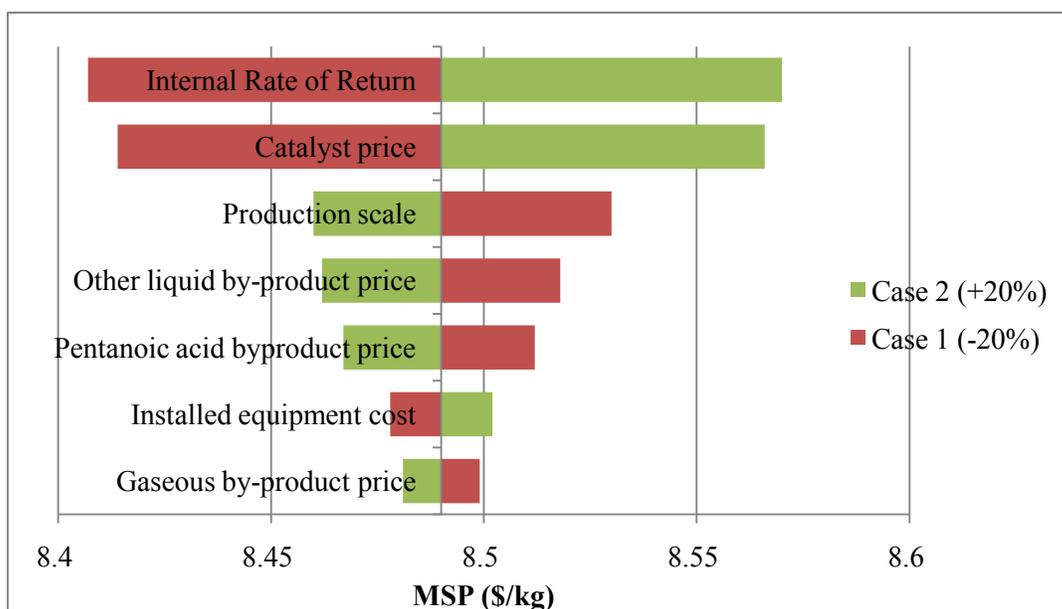


Figure 2.5 Sensitivity analysis for change in MSP

The first chart shows the impact of variations in significant parameters on MSP. Here the impact of Levulinic acid price and DBK yield overwhelm all the other parameters. Hence the second chart from which these two parameters have been excluded, demonstrates more clearly the impact of variations in the other sensitivity parameters.

Bottlenecks and Approach

Figure 2.4 shows that the process is most sensitive to the price of LA feedstock. Thus, a 20% change in the price of feedstock results in about 19% change in the MSP. A price quote of \$3.21 per kg (14) is used for base case. The price and availability of levulinic acid is a major bottleneck in implementation of this process. The Biofine process designed by Biometrics, LLC promises LA production from waste cellulosic biomass at a price of about \$0.09 - \$0.22 per kg (5) when produced on a sufficiently large scale. Commercial availability of LA in large quantities at these low prices can result in a MSP for DBK in the range of \$0.69 - \$0.99 per kg which represents approximately 90% reduction. Such low prices will enable the use of DBK as a commodity scale solvent. However the commercial status of this process is not known. Additionally the economics from the Biofine process (8) assume a price of \$40 per MT (\$36 per short ton) for biomass which will be subject to change based on the demand for biomass. At this price for biomass although the higher LA price of \$0.22 may be plausible, the lower price target of \$0.09 per kg seems difficult to attain. Based on only the yields from Biofine process (5), biomass feed price and by-product credit, LA will cost about \$0.07 per kg. And taking into account other operating expenses and high capital costs for Biofine process, will lead to even higher prices for LA. However with improvements in the process for production of LA we can expect lower prices for LA in future.

The other important parameter affecting the MSP in our process is the DBK total yield. Figure 2.4 shows that a 20% increase in overall DBK yield, accompanied by a decrease in by-product yields, can decrease the MSP by 16% to \$7.1 per kg. As modeled, the current process yields are approximately 98% of the experimental yields (there are minor losses in the purification of DBK) and thus the yield of DBK in the reactor is a major bottleneck that needs to be targeted. A 20% increase in the reaction yield of DBK can reduce the MSP by 14% to \$7.3 per kg. Also the stoichiometric yield of DBK through this pathway is 612 kg/MT and the current process yield is 66% of this maximum. Increase in yields can be possible through improvements in catalyst and optimizing reaction conditions. This will lead to an increase in production of DBK while decreasing by-product formation.

To illustrate the effect of increase in yields, a new catalyst technology in lab scale has resulted in a maximum DBK yield of 85% with no pentanoic acid in product and only easily

separable hexanone and heptanone in product. This eliminates the need for extra purification, thus reducing capital and operating costs. This high yield process results in a 21% lower MSP for DBK of \$6.68 per kg at LA price of \$3.21 per kg. For a LA price of \$0.09 - \$0.22 per kg from the Biofine process, a low DBK MSP of \$0.59 - \$0.85 will be possible. This will certainly increase the competitiveness of DBK as compared to other commodity scale solvents like Methyl Ethyl Ketone.

Even with maximum theoretical yields the current price of levulinic acid, gives a MSP of \$5.81 per kg. If levulinic acid can be purchased for \$0.22/kg, as projected from the Biofine process, a MSP of \$0.79 per kg for pure DBK will be possible with maximum yields. This indicates a steep reduction from the current DBK prices and can also lead to its increased use. Hence, it is evident that only at low LA feedstock price, DBK will be able to compete with MEK which sells for \$0.77 per kg (18).

Degradation, deactivation and regeneration studies have not yet been carried out for the catalyst. Also the composition of catalyst is not known. In such a case there is a significant uncertainty surrounding catalyst requirement and price. A 20% variation in catalyst price under the current assumption, leads to a 1% change in MSP. The catalyst life may be shorter due to faster degradation. In such a case the MSP can rise rapidly due to the increase in the present value of catalyst cost over project lifetime. This also increases the dependency of MSP on catalyst price. However, in this analysis a higher lifespan was assumed to compensate for the unknown composition and thus factoring in a possibly lower price of catalyst when recycled and purchased on large scale. So, in case of decrease in catalyst life from that assumed in the model, the catalyst price might actually be lower than the one currently assumed. With higher rate of catalyst deactivation, more than two reactors might be needed to maintain continuous production. Introduction of an additional reactor can increase the MSP by 2.5%.

Capital costs form a minor fraction of the total product value. A variation of 20% in the production capacity causes a change of only 0.5% in the MSP for DBK. Thus scale up or scale down of this process to suite the availability of feedstock and market demands for DBK, will not have a major impact on the MSP.

The by-products from this process are in the form of a mixed stream. These need to be separated and purified further to obtain a higher value for the by-products. This purification has not been modeled here. Hence a lower value for the by-product streams is assumed. The higher price that can be obtained for purified by-products, needs to justify the additional capital and operating expenses and also subsidize the DBK product price. Given the market price and utility of the by-products, there is a good chance that the MSP for DBK will be reduced in such a case. New technology under development for this process indicates reduction in by-product formation with the presence of only two easily separable ketones as by-products.

Conclusion

This analysis shows that it is possible to produce DBK from biomass-derived raw materials in large quantities that are suitable for applications as a solvent and as a precursor for the production of other chemicals. The need to purify DBK depends on the possible applications. A comparison of two techno-economic models indicates that the additional capital costs for production purification can be justified by the marginally higher MSP of DBK. This is mainly because capital costs constitute a minor fraction of the MSP. In accordance with the general trend for chemical production, the MSP is heavily dependent on the price of LA feedstock and yields of DBK from LA. The large scale availability of cheap levulinic acid feedstock is the key to the feasibility of this process. However the availability of feedstock at such a large scale might be a problem and hence it is essential to investigate economical and large scale production of LA. Improvements in the catalyst and optimization of reaction conditions can result in an increased conversion of LA to DBK and lower the formation of by-products. As indicated by sensitivity analysis and results from new technology under development, even modest increases in yields can significantly lower the MSP.

As modeled, the MSP of DBK produced is comparable to its current price. Lower levulinic acid price can make DBK an economically attractive solvent. But at the 2007 quoted LA price, the MSP is high when with prices for other extensively used petroleum-based ketone solvents like Methyl Ethyl Ketone (\$0.77/kg). However, with large scale availability of low price LA from the Biofine process and increased yields, it would be

possible for DBK to compete on a price basis with solvents like MEK. In such a case, DBK can provide a viable alternative to commodity scale petroleum based solvents.

With new technology already in the lab scale to produce DBK with an 85 % yield, and inexpensive LA from the Biofine process (\$0.09 per kg) it will be possible to produce DBK with a MSP of \$0.68 per kg, thus making it competitive with MEK for solvent utilization. Additionally, this technology allows the formation of an organic stream (free of impurity of pentanoic acid and thus with lower capital costs for production) that easily separates from water and is rich in DBK (92 % in this organic stream) and 8 % of hexanone and heptanone. This stream, without the need of purification (since heptanone and hexanone are also useful), can be used to produce fuels (diesel and gasoline) in one additional reactor. We anticipate that this cheap DBK, with a purity high enough for fuels applications, could be used to produce diesel and gasoline at competitive prices (in the order of \$2-\$3 per gallon) and could be a very promising technology for fuels production from biomass.

Further work is needed to model the purification or utilization of by-products from the process. Further reduction in MSP might be possible, if a higher price for by-products can be obtained, which may justify the additional capital costs required.

The process appears to be feasible as modeled for use of DBK as an industrial chemical. The process could be implemented in a biorefinery complex to enable optimum utilization of feedstock based on market demand. It will also enable utilization of by-products in other processes or purification of by-products to be sold as biobased industrial chemicals. The feasibility of commodity scale solvent and fuel applications by conversion to alkanes through hydrogenation is mainly dependent on the large scale availability of inexpensive Levulinic Acid.

Acknowledgements

This work has been funded by the NSF Engineering Research Center for Biorenewable Chemicals (CBiRC) at Iowa State University and by National Science Foundation grant number CMS0424700. J.C.S.-R. thanks the Spanish Ministry of Science and Innovation for postdoctoral support.

Abbreviations

LA – Levulinic acid

DBK – Dibutyl Ketone (5-Nonanone)

MEK – Methyl Ethyl Ketone

MSP – Minimum Selling Price

MT – Metric Tonnes

MM\$ - Million US Dollars

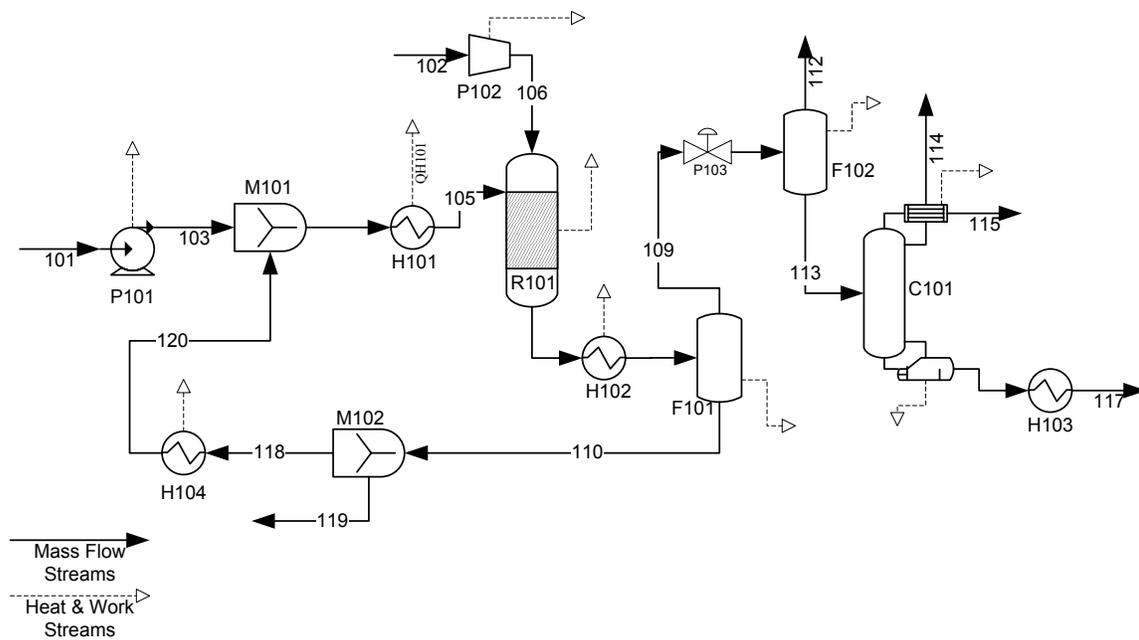
Gal - Gallons

References

1. The Global Oil Depletion Report, Aug 2009, UK Energy Research Centre, available at http://www.ukerc.ac.uk/support/tiki-download_file.php?fileId=283
2. C. H. Christensen, J. Rass-Hansen, C. C. Marsden, E. Taarning and K. Egeblad. 2008 ChemSusChem, 1, 283
3. E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gärtner, J. A. Dumesic. 2008. Catalytic conversion of biomass to monofunctional hydrocarbons and targeted liquid-fuel classes. Science 322, 417–21
4. Timokhin BV, Baransky VA, Eliseeva GD. 1999. Levulinic acid in organic synthesis. Russ. Chem. Rev. 68, 73–84
5. Bozell JJ, Moens L, Elliott DC, Wang Y, Neuenschwander GG, et al. 2000. Production of levulinic acid and use as a platform chemical for derived products. Resources, Conservation and Recycling 28, 227–39
6. O. Casanova, S. Iborra, A. Corma. 2009. Biomass into Chemicals: Aerobic Oxidation of 5-Hydroxymethyl-2-furfural into 2,5-Furandicarboxylic Acid with Gold Nanoparticle Catalysts, ChemSusChem, 2009, in press, DOI: 10.1002/cssc.200900137

7. M. Kitano, F. Tanimoto, M. Okabashi, *Chemical Economy and Engineering Review*, 1975, 7, 25
8. Daniel J. Hayes, Steve Fitzpatrick, Michael H. B. Hayes, Julian R.H. Ross. *The Biofine Process – Production of Levulinic Acid, Furfural, and Formic Acid from Lignocellulosic Feedstocks*. [book auth.] Patrick R. Gruber, and Michael Kamm Birgit Kamm. *Biorefineries - Industrial Processes and Products - Vol. 1*. Weinheim, Germany : Wiley-VCH, 2006, pp. 139-162.
9. Y. L. Hwang and T. C. Bedard, *Ketones in Kirk-Othmer Encyclopedia of Chemical Technology*, 2001, John Wiley and Sons Inc.
10. Juan Carlos Serrano-Ruiz, Drew J. Braden, Ryan M. West and James A. Dumesic, *Angew. Chemie Int. Ed.*, Submitted
11. Aden, A., et al. *Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover*. Golden, CO : NREL, 2002. NREL/TP-510-32438.
12. Max S. Peters, Klaus D. Timmerhaus. *Plant design and economics for chemical engineers*. Boston : McGraw-Hill, 2003. 0072392665.
13. S. W. Fitzpatrick. *Production of levulinic acid by the hydrolysis of carbohydrate-containing materials*. World patent 9640609 to Biofine Incorporated, 1997
14. Linzi Organic Chemical Inc, China. *Levulinic acid price quote*. Price quote. 2009.
15. W. Riemenschneider, *Carboxylic Acids, Aliphatic in Ullmann's Encyclopedia of Industrial Chemistry*, 1993, VCH Publishers Inc
16. Reed Business Information Limited.(ICIS). ICIS. ICIS.com website. [Online] September 3, 2007. [Cited: September 29, 2009.] <http://www.icis.com/v2/chemicals/9076041/methyl-ethyl-ketone/uses.html>.
17. Shanghai Clean Chemical Technology Co. Ltd. *Product Catalog: 5-nonanone*. Shanghai Clean Chemical Technology Web site. [Online] [Cited: June 20, 2009.] http://www.clean-chem.com/sdp/340531/4/pd-1518918/3810906-761674/5-nonanone_Di-n-Butyl_Ketone.html.
18. Keeling, Peter L. *Top 50 Chemicals*. Ames, Iowa, USA : s.n.

19. Kari Skjanes, Peter Lindblad, Jiri Muller. 2007. BioCO₂ – A multidisciplinary, biological approach using solar energy to capture CO₂ while producing H₂ and high value products. *Biomolecular Engineering* 24(4), 405-413
20. Hitoshi Kusama, Kiyomi Okabe, Kazuhiro Sayama, Hironori Arakawa. 2000. Alcohol synthesis by catalytic hydrogenation of CO₂ over Rh-Co/SiO₂. *Applied Organometallic Chemistry* 14(12), 836-840.

Appendix 2.A Process Flow Diagram for Model 'A' (90% purity)**Figure 2.6 Process Flow Diagram for Model A**

Appendix 2.B Process Flow Diagram for Model 'B' (>99% purity)

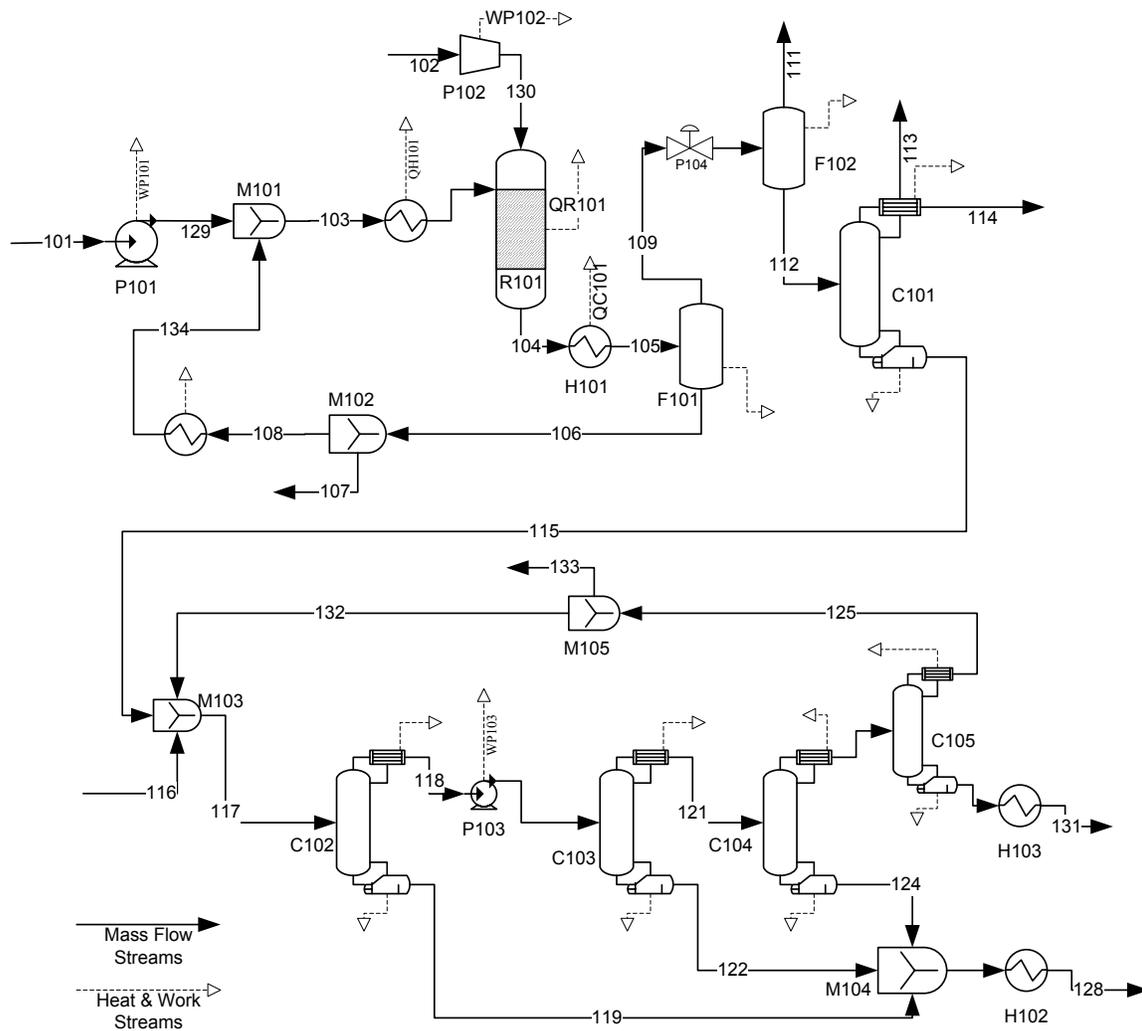


Figure 2.7 Process Flow Diagram for Model B

Appendix 2.C Description of Production Process and Economic Model

Process model

Section1: Feed Mixing and Reaction

This is the raw material input and reaction section for the process. Levulinic acid and Hydrogen gas are the main raw materials required for the process. Levulinic acid is fed as a 50% solution in water to the reactor. Thus water is an additional input. However, water is recycled after separation and purging in later part of the process and hence the feed stream101 contains 20,000 kg/hr of levulinic acid and 6512 kg/hr of water. The feed stream is pressurized to a pressure of 35atm using a centrifugal pump. It is then combined with the recycle water stream, which is heated to 350°C in a multiple pipe heat exchanger with superheated steam. This heated stream is then fed to the reactor. The feed is pre-heated to minimize reactor heating requirements and to facilitate heat integration. Stream 102 serves as the input for hydrogen gas. The gas stream is pressurized to 35atm using a compressor and then fed to the reactor. The pressurization of gas increases its temperature in accordance with ideal gas law. It is then fed to the reactor. The recycled water stream is heated to 90°C before mixing with the feed stream. This is necessary to prevent a significant temperature drop after mixing, which can potentially hamper flow of materials.

Cost estimation and sizing: The purchased equipment price for the mixer, centrifugal pump and compressor are obtained from PT. The mixer is an inline mixer and its cost is based on mass flow rates. Price for centrifugal pump and compressor is based on the volumetric flow rate and outlet pressure desired. The heat exchanger is priced as a multiple pipe heat exchanger with a stainless steel tube and carbon steel shell. The data from Aspen gives the value of heat duty for the exchanger. The surface area is then estimated using the following equation:

$$q = A \times U \times F \times \Delta T_{\log mean}$$

Where q = Heat duty in J/s. Value for “q” is obtained from the process model

U = Overall heat transfer coefficient in J/m².s.K. Values for U are obtained from a standard table in PT and is based on the type of fluid in shell and tube side of the exchanger

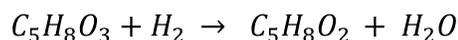
F = Correction factor to account for the type of multipass arrangement. It is obtained from a standard graph in the PT.

$\Delta T_{\log \text{ mean}}$ = Log mean temperature difference. The value for this obtained from the inlet and outlet temperatures of the hot and cold stream. It is calculated using the following equation.

$$\Delta T_{\log \text{ mean}} = \frac{(T_{h,in} - T_{c,out}) - (T_{h,out} - T_{c,in})}{\ln \left[\frac{(T_{h,in} - T_{c,out})}{(T_{h,out} - T_{c,in})} \right]}$$

These terms are used to estimate the heat transfer area requirements for the heat exchangers. Using the calculated area and the pressure data for heat exchangers, the purchased cost is obtained using cost curves in PT.

Reactor: The reaction is carried out in a plug flow tubular reactor. The reactor comprises of two catalyst beds in a steel casing. The reactor is operated so as to achieve near 100% conversion of Levulinic acid to Gamma-valerolactone in the first bed and thereafter 100% conversion of GVL to DBK and other by-products. The complete conversion of LA is necessary to avoid degradation of the subsequent catalyst bed since the second catalyst is sensitive to LA. The following main reactions take place in the reactor:



The overall reaction is:



The reaction conditions are:

Pressure: 34atm

Temperature: 350 °C

Weight Hourly Space Velocity (mass of LA fed per hour/ mass of catalyst used) = 1 hr^{-1}

For the purpose of further analysis the two catalyst beds are considered as one single catalyst bed in the reactor. The reactor is modeled as a yield reactor. The overall reaction produces DBK as the main product and 2-Heptanone, 3-Hexanone, Nonane, Butane and Pentanoic acid as by-products. The lab scale yields were reported as percentage of carbon in feed and have been modified to mass based yields for use in the model. The conversion of LA to DBK and byproducts is as listed in the table below. Along with the compounds

mentioned below, the output from the reactor also consists of un-reacted hydrogen and excess water supplied in the reactor feed.

Table 2.6 Fractional Conversion of Levulinic acid to products

Compounds	% of C in LA feed	Mass % of LA feed in products
5-Nonanone(DBK)	60%	39%
3-Hexanone	8%	6%
2-Heptanone	3%	2%
Nonane	4%	2%
Butane	5%	3%
Pentanoic acid	5%	4%
Carbon di-oxide	15%	27%
Water		16%

Sizing and Cost estimation: The kinetic data for this reaction has not yet been studied. So the reactor has been sized using the values for stream volumetric flow rates, residence time in the reactor and catalyst bulk density considerations. The quantity of catalyst required is determined from the WHSV based on the input LA mass flow rate. It is assumed that two reactors will be needed to maintain continuous operations. After arriving at the reactor size estimate, the reactor cost is estimated following a procedure described in PT. In this estimation PFTR is considered as a reactor with multiple tubes containing catalyst and having a fixed reasonable inner cross sectional area and length. Thus the number of tubes required is based on the reactor volume. The cost is estimated from the price of floating head shell and tube heat exchanger with a similar total heat transfer area. If the area is greater than the maximum available heat exchanger area, then the cost is obtained for two or more smaller exchangers as required to match the total reactor heat transfer area. The catalyst price has been obtained from the approximate price of catalyst used for the lab scale experiments. The catalyst replacement price is incurred after every ten years. Since the composition is unknown, this has been done to take into account the fact that even if the catalyst is replaced early, the active metal which is the most expensive part can be recycled and most of the charges are incurred only for the catalyst support and processing.

Section2: Product Separation

The product stream from the reactor is cooled to 35°C using a multiple pipe heat exchanger and is then flashed in a two-outlet flash separator at 35°C and 34atm pressure. This results mainly in the separation of water which is recycled. About 40% of the water from flash separator needs to be purged out and discarded to waste treatment. This is necessary to prevent a build-up of impurities in the process. The second output from the flash is passed through an expansion valve to reduce the pressure to 12atm and then this stream is again subjected to a second two-output flash separator to separate out the gases, which mainly includes un-reacted hydrogen, carbon di-oxide and butane gas. This stream is considered as gaseous by-product. This flash separator is operated at 35°C and 12atm pressure. The liquid output from the second flash is subjected to distillation to remove remaining by-products from DBK. This distillation involves 20 sieve tray stages and the feed enters above stage 12. The key operating specifications include a molar reflux ratio of 2 and a distillate to feed ratio of 0.3. A partial vapor-liquid condenser is used which operates at 35°C and 2.4atm pressure. Cooling water is used to condense the distillate. The vapor stream mainly includes carbon dioxide and butane gas which is mixed with the gaseous by-product stream obtained from flash separation. The liquid distillate is a mainly a mixture of hexanone, heptanone, butane, nonane and small amounts of pentanoic acid. Multiple pipe heat exchangers as specified in section '1' are used for both condenser and reboiler. The bottoms product includes 90% DBK and about 9.2% of pentanoic acid with other components present in trace quantities. In case of model 'A' the bottoms product is passed through a heat exchanger, where it is cooled to 30°C using cooling water. This output from heat exchanger is the final product stream which is sent to storage. However, in case of model 'B' the bottoms product from distillation passes to the purification section.

Sizing and Cost estimation: The heat exchangers in this section are sized following the procedure described in section '1'. The cost is estimated using purchased cost curves for multiple pipe heat exchangers from PT. The size for flash separators is based on flow rates. The costs for flash separators are obtained from previous NREL study and updated using appropriate scaling exponents. For the distillation column a tray spacing of 0.4m is assumed and the tray sizing routine in ASPEN is used to calculate the column diameter, downcomer

area and velocity and side weir length. The cost estimation is done using ICARUS software which produces detailed estimates based on the specifications provided. The shell and tray material is assumed to be SS304 and the column is designed for a temperature of 300°C and 1250 kPag. All the distillation columns in this analysis are sized using a similar approach.

Section3: DBK purification

This section is only present in model 'B' and is used to further purify DBK. The problem here is that pentanoic acid and DBK have overlapping boiling points. However pentanoic acid is a more polar molecule as compared to DBK. It is theorized that a polar solvent should preferentially dissolve pentanoic acid, thus enhancing the separation process. After simulations with a wide range of polar solvents, methanol was chosen since it gave comparatively favorable results for separation. The bottoms stream from the distillation column in section '2' is mixed with methanol using an inline mixer. Using model analysis tools it was found that presence of 10% methanol in the output stream from the mixer gave the most enhanced separation. Hence, the process was designed to make sure the mixer output stream had 10% methanol. On a steady state basis about 94% of the methanol is recycled after the end of separation sequence and 4% is purged out. The remaining 2% ends up as an impurity in the pentanoic acid stream. At a scale of 20MT/hr of LA about 64kg/hr of methanol is needed.

The impure DBK stream mixed with methanol is passed through a series of three distillation columns. All the columns have 28 stages and are sequenced such that the distillate from the previous is fed as an input to the following column. Total condenser is employed for each column and cooling water is used for condensation. Feed enters the first column C102 above stage 7 and the condenser is maintained at 5atm pressure. The distillate from this column is pressurized to 10atm before feeding to the second column C103 above stage 9. The condenser for C103 is maintained at 10atm. The distillate from C103 is fed to the third column, C104 above stage 6. The distillate from C104 is fed to a methanol recovery column comprising of 10 stages. The distillate from this column consists of 99.3% pure methanol which is recycled after purging. The bottoms stream from the methanol recovery column consists of about 86% pentanoic acid and about 8% DBK. This stream is cooled using a

multiple pipe heat exchanger to 35°C and forms the pentanoic acid by-product stream. The bottoms product from each of the three purification columns consist of >99% pure DBK and are mixed together using an inline mixer. The mixed stream is then cooled using a heat exchanger to 30°C and forms the pure DBK product stream.

Sizing and Cost estimation: The equipments in this section include mixers, distillation columns, heat exchangers and pump. The sizing and cost estimation for each of these is done using the procedure described for similar equipment in the earlier sections.

Process economic model

A discounted cash flow analysis is used to assess the process economics. The process economics are modeled using an Excel spreadsheet. The stream data for material, heat and work streams is imported into the spreadsheet from ASPEN model.

Capital costs: A base stream flow of 500 MT/day LA is used to size and estimate the purchased price for the process equipment. The base stream flow and the purchased equipment prices are entered in 'Access' sheet of the model. This sheet is used to input any other information like chemical prices into the economic model. The equipment list alongwith the base stream flow and purchase price is put together in the 'Equipment' section. Here, new stream flows for current scale of production are imported from Aspen and the equipment costs are scaled accordingly using appropriate scaling indices for the equipment. The scaling equation used is as follows:

$$C = C_0 \times \left(\frac{S}{S_0}\right)^n$$

Here ' S_0 ' is the base scale flow and ' S ' is the new flow, C_0 is the original purchased equipment price based on the original flow and ' n ' is the scaling exponent. This equation scales the equipment price while factoring in the economies of scale that are achieved with increased capacity.

The price estimates are from different points in time depending on the source. Hence these are updated to 2007 prices values using Chemical Engineering Plant cost index. The following formula is used for this purpose:

$$C = C_0 \times \frac{I}{I_0}$$

In this equation ' I_0 ' is the value of index for original year of price quote and ' I ' is the current value of index, in the year of analysis. And C_0 is the original price updated to appropriate scale.

The installation costs are obtained as a percentage of the purchased equipment cost. The installation factor is considered to be a constant for all the equipment. The factor used in this analysis is 2.7 and is based on information for fluid processing plants from PT so as to achieve an overall Lang factor of 4.65. This include charges for equipment installation, instrumentation, piping, electrical connections and building. The installation costs together with the warehouse and site development costs give the total installed equipment cost (TIC) or the total direct plant cost.

The costs for indirect expenses include engineering and supervision, construction expenses, legal and contractor fees. These are estimated as a percentage of the free-on-board (FOB) or the purchased equipment price. Contingency cost is estimated as 20% of the total direct and indirect plant costs. It accounts for unforeseen expenses incurred during the installation and commissioning of plant. The total direct and indirect costs alongwith the contingency give an estimate of the fixed capital investment (FCI) required for the project. Working capital accounts for the startup costs and is estimated as 15% of FCI. The FCI and working capital constitute the total capital investment (TCI) in the project.

Operating costs: These involve costs for raw materials, wastewater treatment, utilities, labor and supervision, maintenance and overhead expenses. Credits from by-products serve to reduce the operating costs. Individual stream flows are used to estimate the costs on an hourly, annual and per gallon basis. The purchase cost for raw materials are obtained from a variety of sources as available or are assumed based on realistic estimates. It is assumed that treatment of wastewater is carried out offsite at an external facility.

A range of by-products are produced alongwith DBK. The liquid by-product stream mainly includes a mixture of heptanone, hexanone, nonane and butane in case of model 'A'. In case of model 'B', pentanoic acid is obtained as a separate stream. The gaseous by-products mainly include hydrogen, carbon-dioxide and butane. The credit for liquid stream is assumed to be about \$500/MT based on possible values of purified products. The credit for

gaseous stream is assumed to be about \$50/MT. The low numbers are assumed to account for possible purification costs. Also in case of gaseous by-products the stream is diluted by the significant amounts of carbon dioxide present. It is assumed that the utilities required are purchased from an external source. All the chemical prices are updated to 2007 dollar value using the Inorganic Chemical index.

The fixed operating costs include labor costs which are estimated based on the number of major operating steps and prevalent labor rate. The labor cost is updated to 2007 level using the Labor index. Besides labor, the overhead costs, maintenance, insurance and taxes are the other costs included in fixed operating costs. The total variable, fixed and utility costs, comprise the operating costs. The cost of catalyst is incurred at every 10 year intervals in the discounted cash flow analysis. Currently it is priced at \$4000 per kg. The long lifetime is assumed to factor in the possible recycle of catalyst materials, which can substantially reduce the recurring cost of catalyst.

The discounted cash flow analysis takes into account cash flows over the entire plant life. In the current analysis the selling price of DBK is iterated at a set internal rate of return to gain a net project value of zero. This price at zero net present value is the Minimum DBK Selling Price (MSP).

Appendix 2.D Mass flows and Costs for key components

Model A:

Stream	Raw Material input		Reactor product	Gaseous by-pr.		Liquid by-pr.		Waste	Product
	101	102		112	114	115	117		
Component Mass Flow									
Levulinic acid	20000	0	0	0	0	0	0	0	0
Hydrogen	0	1736.07	1035.12	1034.2	0.9	0.01	0.01	0.01	0
Water	6512.27	0	23281.75	13.48	1.57	11.98	9767	9767	0
CO2	0	0	5684.79	5500.12	148	32.66	1.67	1.67	0
Dibutyl Ketone	0	0	8168.23	10.59	0	26.25	0	0	8131.4
3-Hexanone	0	0	1151.98	25.81	3.52	1122.33	0	0	0.33
2-Heptanone	0	0	417.39	3	0.4	399.86	0	0	14.14
Nonane	0	0	492.51	4.17	0.58	475.01	0	0	12.75
Butane	0	0	626.08	418.84	46.1	161.13	0	0	0
Valeric acid	0	0	880.68	0.81	0.01	55.68	0.09	0.09	823.97
Mole Flow	533.73	861.2	2030.8	646.35	4.73	23.32	542.19	542.19	65.46
Mass Flow	26512.3	1736.07	41738.52	7011.02	201	2284.9	9768.8	9768.8	8982.6
Volume Flow	416.51	178694	49199.01	22725.1	819	50	165.41	165.41	181.44
Temperature	293.15	303.15	623.15	308.15	308	308.15	308.15	308.15	303.15
Pressure	2	2	34.02	12	2.4	2.4	34	34	1
Mass Density	1.06	0	0.01	0.01	0	0.76	0.98	0.98	0.83

Table 2.7 Mass Flow and properties of key streams for Model A

Model B:

Stream	Raw Material Inputs			Reactor product	Gaseous by-pr.			Liquid by-pr.	Valeric acid(by-pr.)			Waste Streams			Product
	101	102	116		104	111	113		114	131	107	133	128		
Component Mass Flow															
Levulinic acid	20000	0	0	0	0	0	0	0	0	0	0	0	0	0	
Hydrogen	0	1736.07	0	1035.14	1034.22	0.9	0.01	0	0	0	0	0	0	0	
Water	1397.32	0	0	23282.26	13.48	1.57	11.98	0	4651.1	0	0	0	0	0	
CO2	0	0	0	5684.91	5500.24	148	32.66	0	0.8	0	0	0	0	0	
Dibutyl Ketone	0	0	0	8168.41	10.59	0	26.26	83.97	0	0	0	0	0	8047.6	
3-Hexanone	0	0	0	1152.01	25.81	3.52	1122.35	0.33	0	0	0	0	0	0	
2-Heptanone	0	0	0	417.39	3	0.4	399.87	14.13	0	0	0	0	0	0	
Nonane	0	0	0	492.53	4.17	0.58	475.02	12.45	0	0.3	0	0	0	0	
Butane	0	0	0	626.09	418.85	46.11	161.14	0	0	0	0	0	0	0	
Valeric acid	0	0	0	880.7	0.81	0.01	55.69	787.63	0.04	0	0	0	0	36.34	
Methanol	0	0	58.93	0	0	0	0	19.77	0	39.2	0	0	0	0	
Mole Flow	249.8	861.2	1.84	2030.85	646.37	4.73	23.32	9.14	258.19	1.22	0	0	0	56.93	
Mass Flow	21397.3	1736.07	58.93	41739.45	7011.17	201.1	2284.97	918.27	4651.9	39.5	0	0	0	8083.9	
Volume Flow	323.14	178694	1.25	49200.11	22725.6	818.5	50	16.62	78.77	1.01	0	0	0	165.4	
Temperature	303.15	303.15	303.2	623.15	308.15	308.2	308.15	303.15	308.15	405	0	0	0	303.15	
Pressure	1	2	2	34.02	12	2.4	2.4	10	34.02	9	0	0	0	1	
Mass Density	1.1	0	0.79	0.01	0.01	0	0.76	0.92	0.98	0.65	0	0	0	0.81	

Table 2.8 Mass Flow and properties of key streams for Model B

Cost of Chemicals:

Table 2.9 Cost of Chemicals

Chemical	Price	Year of Quote
Levulinic acid	3.21\$/kg	2009
Hydrogen	4.32 \$/1000ft ³	2008
Methanol	55 cents/gal	2008
Di-Butyl Ketone	9.07 \$/kg	2009
Gaseous by-product credit	50 \$/MT (assumed)	2007
Liquid by-product credit	500 \$/MT (assumed)	2007
Pentanoic acid(Valeric acid)	1 \$/kg (assumed)	2007

Appendix 2.E List of Equipment and Cost estimates

Model A:

Table 2.10 Equipment list and Installed cost for Model A

Equipment Number	Number Required	Equipment Name	Installed Cost in 2007\$
P101	1	Feed Pump	\$158,651
M101	1	Feed Recycle Mixer	\$22,812
H101	1	Reactor Feed Heater	\$96,925
R101	2	Reactor	\$9,576,990
P102	1	Hydrogen Feed Compressor	\$50,276
H102	1	Product Cooler	\$400,890
F101	1	Water Flash Separator	\$148,155
P103	1	Pressure release valve	\$67,137
F102	1	Gas flash separator	\$58,210
C101	1	Product Separation Column	\$1,834,879
RBC101	1	Column Reboiler	\$88,100
CDC101	1	Column condenser	\$92,566
H103	1	Product Cooler	\$83,695
M102	1	Recycled water purge	\$22,811
H104	1	Recycled water heater	\$74,900
		Total cost	\$12,776,998.31

Model B:

Table 2.11 Equipment list and installed cost for Model B

Equipment Number	Number Required	Equipment Name	Installed Cost in 2007\$
P101	1	Feed Pump	\$59,321
M101	1	Feed Recycle Mixer	\$28,231
R101	2	Reactor	\$9,115,373
P102	1	Hydrogen Feed Compressor	\$50,903
H101	1	Product Cooler	\$1,577,911
F101	1	Water Flash Separator	\$135,147
P104	1	Pressure release valve	\$63,904
F102	1	Gas flash separator	\$58,133
C101	1	Hydrocarbon separation column	\$1,759,018

Equipment Number	Number Required	Equipment Name	Installed Cost in 2007\$
RBC101	1	Column Reboiler	\$35,392
CDC101	1	Column condenser	\$56,038
M102	1	Recycled water purge	\$21,778
H104	1	Recycled water heater	\$29,492
M103	1	Methanol mixer	\$14,529
C102	1	Nonanone purification column	\$997,191
RBC102	1	Column Reboiler	\$35,513
CDC102	1	Column condenser	\$58,801
P103	1	Column feed pump	\$22,050
C103	1	Nonanone purification column	\$728,565
RBC103	1	Column Reboiler	\$32,547
CDC103	1	Column condenser	\$32,212
C104	1	Nonanone purification column	\$748,844
RBC104	1	Column Reboiler	\$33,647
CDC104	1	Column condenser	\$36,610
C105	1	Methanol recovery column	\$350,086
RBC105	1	Column Reboiler	\$30,435
CDC105	1	Column condenser	\$34,011
H103	1	Pentanoic acid cooler	\$26,087
M105	1	Methanol purge	\$4,849
M104	1	Product Mixer	\$12,932
H102	1	Product Cooler	\$32,536
		Total Installed cost	\$ 16,222,090.66

Appendix 2.F Sensitivity parameters and values

Model A:

Table 2.12 Sensitivity parameters and values

Parameter	Base Case		
	Value	Units	MSP(\$/kg)
LA price (0.73:3.21:3.85)	3.21	\$/kg	7.701
Liquid byproduct price (0.5 ± 20%)	0.5	\$/kg	7.701
Gaseous by-product price (0.05 ± 20%)	0.05	\$/kg	7.701
Catalyst cost (\$1K:\$4K:\$4.8K)	4000	\$/kg	7.701
Catalyst life (2:10:12 yrs)	10	years	7.701
DBK yield (449kg/MTLA ± 20%)	449	kg/MT LA	7.701
No. of reactors(1:2:3)	2		7.701
Production capacity (20MT/hr ± 20%)	20	MT LA/hr	7.701

Parameter	Case 1			
	Value	Units	MSP(\$/kg)	% change
LA price (0.73:3.21:3.85)	3.852	\$/kg	9.153	18.85%
Liquid byproduct price (0.5 ± 20%)	0.60	\$/kg	7.676	-0.32%
Gaseous by-product price (0.05 ± 20%)	0.06	\$/kg	7.693	-0.10%
Catalyst cost(\$1K:\$4K:\$4.8K)	4800	\$/kg	7.77	0.90%
Catalyst life(2:10:12 yrs)	12.00	years	7.684	-0.22%
DBK yield (449kg/MTLA ± 20%)	538.8	kg/MT LA	6.486	-15.78%
No. of reactors(1:2:3)	3		7.895	2.52%
Production capacity (20MT/hr ± 20%)	24	MT LA/hr	7.675	-0.34%

Parameter	Case 2			
	Value	Units	MSP	%change
LA price (0.73:3.21:3.85)	0.73	\$/kg	2.092	-72.83%
Liquid byproduct price(0.5 ± 20%)	0.4	\$/kg	7.726	0.32%
Gaseous by-product price(0.05 ± 20%)	0.04	\$/kg	7.709	0.10%
Catalyst cost(\$1K:\$4K:\$4.8K)	1000	\$/kg	7.445	-3.32%
Catalyst life(2:10:12 yrs)	2	years	8.598	11.65%
DBK production (215MT/day ± 20%)	359.2	kg/MTLA	9.524	23.67%
No. of reactors(1:2:3)	1		7.508	-2.51%
Production capacity (20MT/hr ± 20%)	16	MT LA/hr	7.736	0.45%

Model B:

Parameter	Base Case		
	Value	Units	MSP(\$/kg)
LA price (0.73:3.21:3.85)	3.21	\$/kg	8.49
Liquid byproduct price (0.5 ± 20%)	0.5	\$/kg	8.49
Gaseous by-product price (0.05 ± 20%)	0.05	\$/kg	8.49
Catalyst cost(\$1K:\$4K:\$4.8K)	4000	\$/kg	8.49
Catalyst life(2:10:12 yrs)	10	years	8.49
DBK yield (405kg/MT ± 20%)	405	MMgal/yr	8.49
No. of reactors(1:2:3)	2		8.49
Production capacity (20MT/hr ± 20%)	20	MT LA/hr	8.49

Parameter	Case 1			
	Value	Units	MSP	% change
LA price (0.73:3.21:3.85)	3.852	\$/kg	10.1	18.96%
Liquid byproduct price (0.5 ± 20%)	0.60	\$/kg	8.462	-0.33%
Gaseous by-product price (0.05 ± 20%)	0.06	\$/kg	8.481	-0.11%
Catalyst cost(\$1K:\$4K:\$4.8K)	4800	\$/kg	8.566	0.90%
Catalyst life(2:10:12 yrs)	12.00	years	8.471	-0.22%
DBK yield (405kg/MT ± 20%)	486.000	kg/MT LA	7.076	-16.65%
No. of reactors(1:2:3)	3		8.703	2.51%
Production capacity (20MT/hr ± 20%)	24	MT LA/hr	8.46	-0.35%

Parameter	Case 2			
	Value	Units	MSP	%change
LA price (0.73:3.21:3.85)	0.73	\$/kg	2.269	-73.27%
Liquid byproduct price(0.5 ± 20%)	0.4	\$/kg	8.598	1.27%
Gaseous by-product price(0.05 ± 20%)	0.04	\$/kg	8.499	0.11%
Catalyst cost(\$1K:\$4K:\$4.8K)	1000	\$/kg	8.206	-3.35%
Catalyst life(2:10:12 yrs)	2	years	9.485	11.72%
DBK yield (405kg/MT ± 20%)	324	kg/MT LA	10.612	24.99%
No. of reactors(1:2:3)	1		8.277	-2.51%
Production capacity (20MT/hr ± 20%)	16	MT LA/hr	8.53	0.47%

Appendix 2.G Summaries of Process Engineering Analysis

Model A

Dibutyl Ketone Production Process Engineering Analysis		
Production of 90% pure DBK Conversion of Levulinic acid to GVL and then DBK in one reactor All Values in 2007\$		
Minimum Dibutyl Ketone Selling Price \$24.05 per gallon		90% purity
\$7.701 per kg		
Dibutyl Ketone Production (MM Gal. / Year) 24.2		
Dibutyl Ketone production (MT/Year) 75453.5		
Dibutyl Ketone Yield (Gal / MT Feedstock) 143.8		
Feedstock Cost \$/MT \$3,210		
Internal Rate of Return (After-Tax) 10%		
Equity Percent of Total Investment 100%		
Capital Costs		Operating Costs (cents/gal DBK)
Reactor	\$9,577,058	Feedstock 2232.4
Separation system	\$2,400,000	Other Raw Materials 8.2
Other	\$800,000	Waste Disposal 0.0
Total Installed Equipment Cost	\$12,777,058	Utilities 41.5
		Fixed Costs 15.5
Added Costs	\$9,222,942	By-product credits -52.3
(% of TPI)	42%	Capital Depreciation 4.6
Total Project Investment	\$22,000,000	Average Income Tax 16.38
		Average Return on Investment 139.2
		Operating Costs (\$/yr)
Installed Equipment Cost/Annual Gallon	\$0.53	Feedstock \$539,300,000
Total Project Investment/Annual Gallon	\$0.91	Other Raw Materials \$2,000,000
Loan Rate	N/A	Waste Disposal \$9,047
Term (years)	N/A	Utilities \$10,000,000
Capital Charge Factor	1.759	Fixed Costs \$3,700,000
		By-product credits -\$12,600,000
APV of catalyst cost(MM\$)	198	Capital Depreciation \$1,100,000
Byproduct Gases(MT/yr)	60581.8	Average Income Tax \$4,000,000
Approx sale price(\$/kg)	\$0.05	Average Return on Investment \$33,600,000
Revenue(MM\$/yr)	\$3.03	
		Specific Operating Conditions
Maximum Yields (100% of Experimental)		Levulinic acid feed(MT/day) 480
DBK Production (MM Gal/yr)	24.5	Approx biomass input (MT/day) 2000
Experimental Yield (Gal/MT)	145.8	WHSV(kg LA per hour/kg catalyst) 1.0
Current Yield (Actual/Experimental)	98.6%	Catalyst requirement(MT) 40.0

Model B

Dibutyl Ketone Production Process Engineering Analysis			
Production of 99.5% pure DBK Conversion of Levulinic acid to GVL and then DBK in one reactor All Values in 2007\$			
Minimum Dibutyl Ketone Selling Price \$26.18 per gallon		99.5% purity	
\$8.490 per kg			
Dibutyl Ketone Production (MM Gal. / Year) 22.1 Dibutyl Ketone Production (MT/ Year) 68035.9 Dibutyl Ketone Yield (Gal / MT Feedstock) 131.3 Feedstock Cost \$/MT \$3,210 Internal Rate of Return (After-Tax) 10% Equity Percent of Total Investment 100%			
Capital Costs		Operating Costs (cents/gal DBK)	
Reactor	\$9,100,000	Feedstock	2444.5
Separation system	\$2,100,000	Other Raw Materials	10.4
Purification system	\$3,198,911	Waste Disposal	0.02
Other	\$1,823,180	Utilities	47.5
Total Installed Equipment Cost	\$16,200,000	Fixed Costs	27.4
		By-product credits	-91.8
Added Costs	\$11,400,000	Capital Depreciation	6.3
(% of TPI)	41%	Average Income Tax	18.8
Total Project Investment	\$27,600,000	Average Return on Investment	155.0
		Operating Costs (\$/yr)	
Installed Equipment Cost/Annual Gallon	\$0.73	Feedstock	\$539,300,000
Total Project Investment/Annual Gallon	\$1.25	Other Raw Matl. Costs	\$2,300,000
Loan Rate	N/A	Waste Disposal	\$4,308
Term (years)	N/A	Utilities	\$10,500,000
Capital Charge Factor	1.442	Fixed Costs	\$6,000,000
		By-product credits	-\$20,300,000
APV of catalyst cost (MMS)	198.0	Capital Depreciation	\$1,400,000
By-product gases (MT/yr)	\$60,583.10	Average Income Tax	\$4,200,000
Approx sale price (\$/kg)	\$0.05	Average Return on Investment	\$34,200,000
Revenue (MMS/yr)	\$3.03	Specific Operating Conditions	
		Levulinic acid feed (MT/day)	480.0
Maximum Yields (100% of Experimental)		Approx. biomass input(MT/day)	2000.0
DBK Production (MM Gal/yr)	22.5	WHSV(kg LA per hour/kg catalyst)	1.0
Experimental Yield (Gal/MT)	133.7	Catalyst requirement(MT)	40.0
Current Yield (Actual/Experimental)	98%		

Chapter 3: Techno-economic analysis of Dimethylfuran (DMF) and Hydroxymethylfurfural (HMF) production from pure fructose in catalytic processes

A paper to be submitted to the Journal of Bioresource Technology

Feroz Kabir¹, Akshay Patel¹, Juan Carlos Serrano-Ruiz², James A. Dumesic², Robert P. Anex¹

¹Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA 50011

²Department of Chemical and Biological Engineering, University of Wisconsin, 1413 Engineering Drive, Madison, WI 53706

Abstract

Techno-economic studies of hydroxymethyl-furfural (HMF) and dimethyl-furan (DMF) production processes from fructose are performed based on published laboratory results. The technologies are at an early stage of development and thus assumptions are made to simplify the models which might introduce uncertainties in the analysis. The processes are modeled as modules of a conceptual bio-refinery. HMF and DMF production processes are divided into four and six processing areas respectively that include synthesis and purifications sections. HMF process has a biphasic continuously stirred tank reactor (CSTR) and DMF process has additional 3-train fixed bed catalytic (PFTR). The processing capacities are assumed 300 MT/day of fructose and the plants will operate for 20 years. Installed equipment costs are estimated (in 2007\$ values) as MM\$102.4 for HMF and MM\$121.9 for DMF processes respectively. The DMF process requires CuRu/C catalyst and its life is assumed 2 years. Catalyst cost is estimated as MM\$36.4 for the first charge and replacement cost of \$258,500/2-years. Cost analysis is performed following discounted cash flow method. The Minimum Selling Prices (MSP) for HMF and DMF are obtained as

\$5.03/Gal and \$7.63/Gal respectively. Sensitivity analysis has been performed to study the relative impact of assumptions on minimum HMF and DMF selling prices. The most significant parameters are feedstock cost, product yields, byproduct prices, catalyst cost and total purchased equipment costs. Process and economic uncertainties can be reduced by incorporating better performance (through laboratory and pilot trials) and cost data which may significantly reduce the currently estimated minimum selling prices.

Keywords: Bio-fuel, DMF, HMF, Lignocellulosics, Minimum selling price, Techno-economics

Introduction

Diminishing petroleum resources and increasing demand for energy and industrial chemicals has resulted in the quest for development of sustainable alternative approaches to produce transportation fuel and industrial chemicals. Over the past decades significant improvements in technology have led to commercial production of corn ethanol as an alternative transportation fuel to gasoline. In USA, ethanol production increased from 190 MMGal in 1980 to 4.8 Billion Gal in 2006 and is expected to reach 15 Billion gallon of corn ethanol, and 21 Billion gallons of advanced biofuels in 2022 (1, 2, 3). Currently ethanol production in the USA relies almost entirely on corn feedstock. In 2006, ethanol industry consumed nearly 20% of the U.S. corn crop (3). The demand of corn for the ethanol production raises the ethical debate of 'food vs fuel'. Therefore, the conversion of non-food biomass to fuel is the preferred long term strategy. Advanced biofuels are mandated to be derived from lignocellulosics as an alternative to food grain. Lignocellulosics are regarded as sustainable and environmentally benign source of feedstock (4). The advanced biofuels include cellulosic ethanol, butanol, furan, biogasoline and other advanced transportation biofuels. Although ethanol is the predominant biofuel, it is not regarded as an ideal fuel due to its inferior physical properties (volatility and hygroscopic properties) and low energy density. Moreover, ethanol is being produced in biochemical processes where enzyme, yeast or bacteria are used, which is not compatible with the existing infrastructure of petrochemical industries.

Lignocellulosic biomass is a heterogeneous substrate, its physical and chemical properties vary with its sources. The potential feedstocks are corn stover, energy crops,

agricultural and forest residues, and municipal wastes. The industries are interested in a process which is flexible enough to handle feedstock variations and should be able to employ several conventional technologies to produce biofuels and chemicals as products and byproducts. Currently various research groups are working on better quality biofuel following conventional process approaches and claiming some level of success at bench and pilot scale operations (5, 6, 7, 8). Dr. Dumesic and colleagues from the University of Wisconsin (6, 9) have demonstrated catalytic conversion of fructose to HMF, which is a suitable substitute for building blocks derived from petrochemicals in the production of industrial chemicals, polymers and fine chemicals. Dr. Dumesic and colleagues have further processed HMF, in a conventional fixed bed catalytic PFTR, to produce DMF. Compared to ethanol, DMF has better fuel, transportation, storage and blending properties making it an attractive bio-based liquid fuel (6). It can also be a renewable source of furan based compounds which have widespread use in the industrial solvent and pharmaceutical industry. Additionally the catalytic conversion process is similar to conventional petrochemical production and purification unit operations so these methods may benefit from extensive design and operation experience and may utilize infrastructure developed in the petrochemical industry. Our aim is to evaluate the techno-economic feasibility of HMF and DMF production processes from fructose as modules of a conceptual biorefinery.

Materials and Methods

Detailed block diagrams of HMF and DMF production processes based on published literature (6) are developed and shown in Figures 3.1 and 3.2 respectively. At present, the technologies are at the early stage of development. Thus the technical information is obtained primarily from a single source (6, 9, 10). The information on operating conditions and design parameters of major unit operations for some of the most critical areas is limited. Thus assumptions are made to simplify the processes which might introduce uncertainties into our analysis.

Equipment price quote and installation factors are obtained from public databases (11, 12, 13). Individual unit operations are scaled and cost is estimated following six-tenth

exponential correlation (13). The scaled equipment cost is then indexed to 2007\$ values (14). Cost analysis is performed following NREL report (11) and published literature (13) approach with modified terminologies. Total Installed Cost (TIC) is defined as the sum of Total Purchased Equipment Cost (PEC), Installation Cost (39% of PEC), Instrumentation (43% of PEC), Piping (31% of PEC), Electrical (10% of PEC), Buildings (15% of PEC), Yard Improvements (12% of PEC), and Service Facilities (55% of PEC). The Total Indirect Plant Cost (TIPC) is defined as the sum of Engineering and Supervision cost (32% of PEC), Construction Expenses (34% of PEC), Legal Expenses (4% of PEC), Contractors Fees (19% of PEC), and Contingency (35% of PEC). Fixed Capital Investment (FCI) is the sum of Total Installed Cost and Total Indirect Plant Cost. Startup Cost is assumed 10% of FCI. Total Capital Investment (TCI) is the sum of FCI and Startup Cost. Discounted cash flow analysis has been performed to obtain the Minimum Selling Price of HMF and DMF for an n^{th} plant. The n^{th} plant is defined as that a similar plant was previously built and operated without unexpected delays in startup and capacity loss. The discounted cash flow analysis program iterates on the HMF and DMF selling prices until the net present value of the projects equal to zero (11).

For the present study, utilities and wastewater treatment plants are not included, instead it is assumed that utilities are purchased and wastewater is treated by a third party at a fixed price per unit volume (13). A range of additional assumptions have been made. The major assumptions are:

- The plant size is 300 MT/day of fructose. Fructose is available at a fixed cost of \$300/MT.
- Levulinic and formic acids are the 2 byproducts produced in biphasic CSTR. The market value of levulinic acid is assumed at \$300/MT (100% purity basis) same as that of fructose. The process uses NaCl to enhance HMF transport from aqueous to organic phase in the CSTR. It is assumed that a CSTR with attached filter will be able to retain most of the NaCl in the reactor.
- The byproducts in PFTR were unidentified (6) so they are referred to as unknown byproducts and we assume their physical properties to be same as

that of DMF. The unidentified byproducts have low quality fuel value with market price of \$50/MT (same as that of biomass or coal price).

- Surrogate compounds were selected (based on physical properties) for the missing compounds in the Aspen database such as HMF and DMF.
- Product yields, selectivity and operating conditions are obtained from published literature (6).
- CuRu/C-catalyst loading is estimated based on published bench scale data (6) and obtained as 21.9 MT/charge. The catalyst cost is estimated as the sum of precious metals cost (15) plus \$11/kg of catalyst for support and manufacturing. The catalyst life is considered as 2 years. It is assumed that the catalyst manufacturer will be able to recover 99.99% of the metals in the spent catalyst. Therefore, after every 2 years only the cost of catalyst support, makeup metals and manufacturing cost would be required which is estimated as \$258,500/charge. At the end of 20 years of plant life the catalyst metals will be recovered and their values are discounted to 2007\$ value.
- Cost of other raw materials (indexed to 2007\$ vales) are: \$1350/MT butanol, \$93.7/MT of HCl, \$160/MT of NaCl, \$550/MT of H₂, \$1.1/MT of water.
- Butanol in product and byproduct streams is considered as butanol loss.
- Plant is depreciated in 7 years with zero salvage value. Depreciation cost is estimated following IRS Modified Accelerated Cost Recovery System (MARCS). The plant life is 20 years.
- The investment is assumed 100% equity financed, and Internal Rate of Return (IRR) is 10%.

Sensitivity analysis has been performed to study the robustness of MSP for HMF and DMF. The parameters that introduce uncertainties in process operations and economics are subjected to sensitivity analysis. Two point values are selected to study the effect of upper and lower limits of the parameters and are designated as scenario-1 and scenario-2.

Process Description and Flow Diagram

HMF production process

Figure 3.1 shows the detailed block diagram of HMF production process. HMF is produced from fructose in a biphasic reactor where water and butanol are used to create a 2-phase system. The reactions take place at 453 K in liquid phase for 3 minutes. The aqueous phase favors the conversion of fructose to HMF. In the aqueous phase, fructose, HCl and NaCl are introduced. HCl acts as catalyst for the conversion of fructose to HMF. In the aqueous phase, HMF degrades to levulinic and formic acids. The extent of degradation depends on the process parameters and reaction severity. In the biphasic reactor, HMF is continuously extracted into the organic phase, this reduces HMF degradation to byproducts and increases yield and selectivity. NaCl enhances transport of HMF from aqueous to organic phase. The ratio of butanol to aqueous stream is maintained as 3.2 vol/vol (8). The product stream is partially separated in area 200. Formic acid in the product stream is distilled in a distillation column as a dilute wastewater stream and sent to wastewater treatment and the bottom stream is sent to decanting. In decanting section, HMF is separated from fructose and levulinic acid by washing with water. HMF in the organic phase is then purified in Area 300. Levulinic and unconverted fructose are separated in Area 400. The recovered fructose is recycled to CSTR, and the levulinic acid with purity of nearly 98% is sent to storage tank.

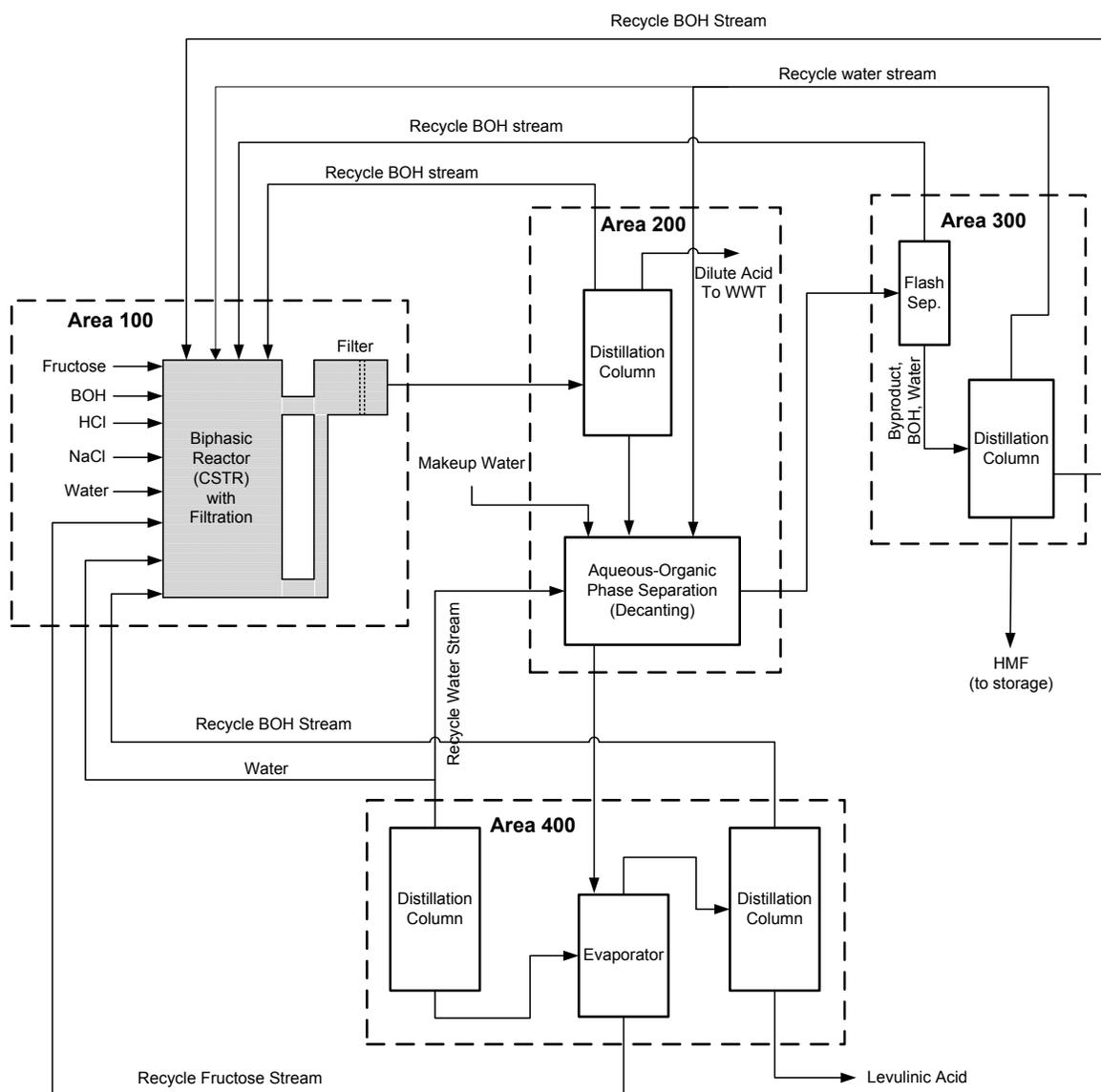


Figure 3.1 HMF production process block diagram

DMF production process

Figure 3.2 shows the detailed process block diagram of DMF production from fructose via HMF. HMF is produced in a biphasic reactor in Area 100. CSTR products are partially separated in Area 200. HMF in organic rich phase is then flashed to remove excess butanol, the remaining stream is vaporized at 493K and 250 psi in Area 300. The vapor is

then sent to PFTR where hydrogen is added for the conversion of HMF to DMF in presence of CuRu/C catalyst. The process adopts a 3-train PFTR reactor configuration with one on-stream reactor and two on regeneration. The reactor is operated at 100% conversion of HMF. An unidentified byproduct is also produced in the reactor. DMF is separated in Area 400 via flash separator and distillation columns. The bottom stream from distillation column in Area 400 is further distilled in Area 600 where byproduct, butanol and water are separated and recycled. The aqueous stream from Area 200 is evaporated and distilled to separate levulinic acid, fructose, butanol and water. Fructose, water and butanol are recycled to the process.

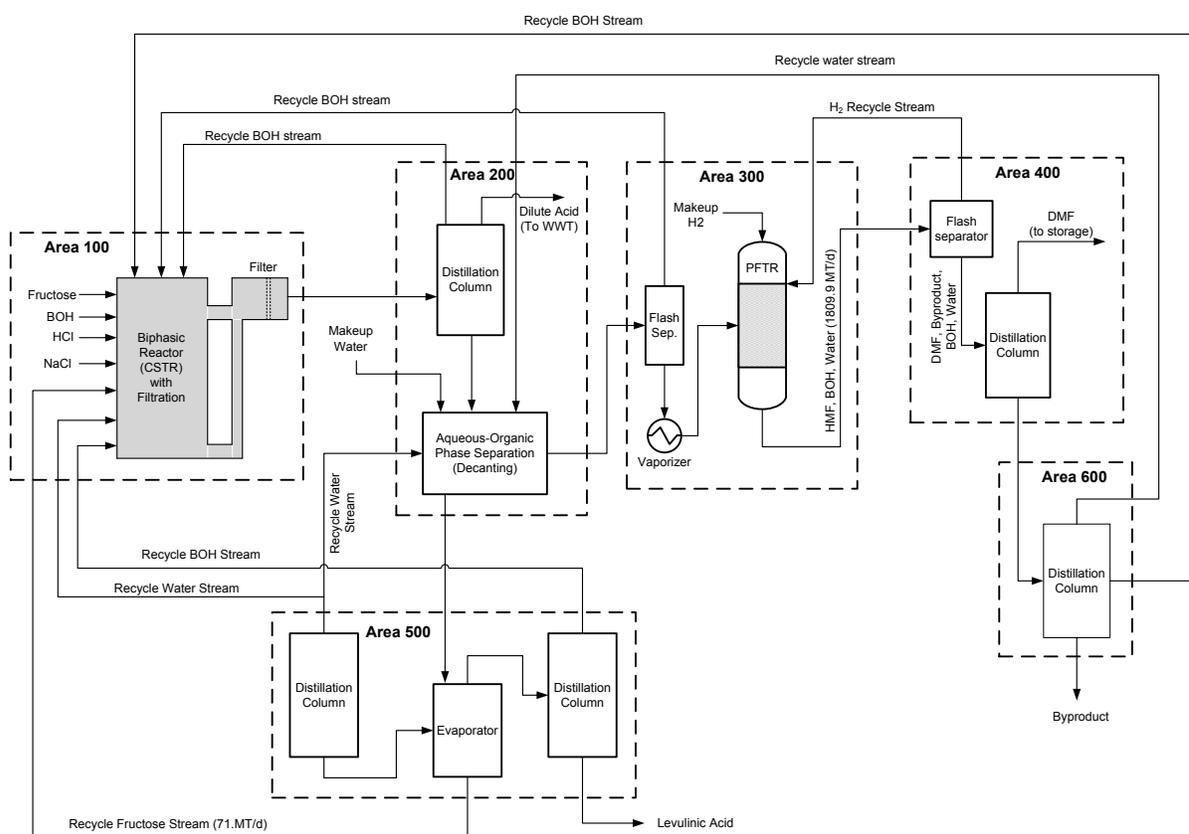


Figure 3.2 DMF production process block diagram

Results and Discussion

HMF production

The simulated material balance for the HMF production process is shown in Table 3.1. For a plant capacity of 300MT/day of fructose, nearly 174 MT/day of HMF (99% pure) and 34 MT/day of levulinic acid (98% pure) are produced as product and byproduct respectively. The process also produces formic acid as byproduct. However, the concentration of formic acid in the aqueous stream is so low that its purification becomes rigorous and cost intensive thus the stream is sent to wastewater treatment.

Table 3.1 Feed and product flow rates for HMF production process

Feed Stream		Product Stream		
Raw materials*	Flow rates (MT/day)	Products / byproduct	Flow rate (MT/day)	Purity (%)
Fructose	300	HMF	174.2	99.34
Butanol	1.37	Levulinic Acid	33.5	97.66
HCl	3.83			
Water	461.6			
NaCl	0.40			

* raw materials are assumed 100% pure

The annual production of HMF as modeled is 61000 MT. For a potential use in production of 2,5-furan di-carboxylic acid(FDCA) (16), the market for HMF will be comparable with the market for terephthalic acid which exceeds 4 MMT in North America (17).

Area wise installed equipment cost indexed to 2007\$ value (14) is shown in Table 3.2. Total installed equipment cost for the base case scenario is estimated as MM\$102.4. The most expensive process areas are identified as Area 200 (aqueous-organic phase separation section) and Area 300 (levulinic acid and fructose separation section) as 28 and 65% of total installed equipment cost respectively. Area 200 has a series of decanters and distillation columns. In Area 400, fructose and levulinic acid are separated through evaporators and distillation columns.

Table 3.2 Installed equipment cost for HMF production

Process Sections (Areas)	Installed equipment cost	
	(MMS)	(%)
Biphasic reactor section (Area 100)	1.86	1.82
Partial separation section (Area 200)	28.13	27.48
HMF purification section (Area 300)	7.24	7.07
Levulinic acid and fructose separation section (Area 400)	65.14	63.63
Total	102.37	100

The total purchased equipment cost for the HMF production process has been estimated as MM\$33.6 in 2007\$ value. The total installed cost, total indirect plant cost and startup costs are obtained as MM\$102.4, MM\$41.6 and MM\$14.4 respectively. The total capital investment for the project is estimated as MM\$158.4. The Minimum Selling Price for HMF is obtained as \$5.03/gal or \$1.07 per kg (in 2007\$ value). This price is low enough to place HMF in the commodity chemicals category for use in a range of other chemical production processes. However, it is quite high for subsequent production of FDCA to replace Terephthalic acid which sells for around \$0.69/kg (17). Summary of the analysis results is shown in Appendix 3B.

The annual HMF production and yield are 13 MMGal and 123.4 Gal/MT of fructose respectively. The current process yield is obtained as 87% of experimental yields, which means that approximately 1.8MMGal of HMF is lost in various process waste streams. This loss is mostly due to the reduced effectiveness of unit operations at large scale. If the unit operations and operating conditions can be improved to reach 100% process yield then 14.8 MMGal of HMF could be produced which would reduce the MSP of HMF to \$4.4/Gal or \$0.94/kg.

Sensitivity analysis has been performed to study the relative significance of economic and process parameters on MSP. Based on our perception of uncertainty in the assumptions, the sensitivity of HMF MSP is measured for a 20% change in the values for critical parameters (Figure 3.3).

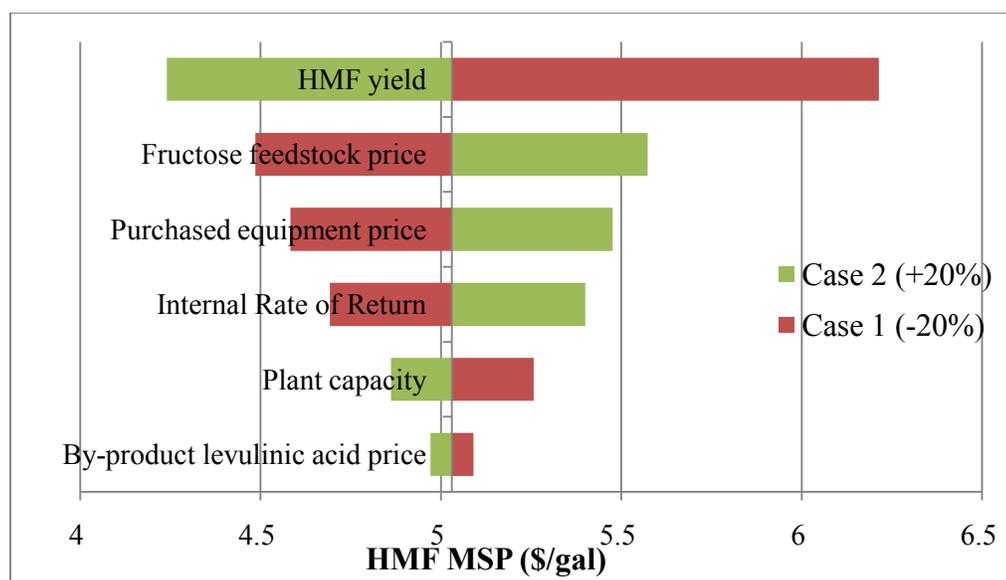


Figure 3.3 Sensitivity analysis on minimum HMF selling price

From the graph it is evident that the yield of HMF from fructose is the most significant parameter affecting the MSP. A 20% increase in HMF yield can result in a 15.7% decrease in the MSP to \$5.03/gal. The current process yield of 123.4 gal/MT is 83% of theoretical maximum. The major factor affecting the yield of HMF and thus a bottleneck, is the extraction of HMF into the organic phase after formation in aqueous phase. More efficient extraction of HMF will minimize the conversion of HMF to by-products, thus increasing yields. Enhancing removal of HMF from the aqueous phase will also allow longer reaction times to increase conversion of fructose which is at 75% in the current model (9). The next factor affecting yield is the selectivity for HMF. Alternative chemical catalyst based processes should be investigated to address problems with conversion, selectivity and HMF extraction.

Given the significance of HMF yield, as expected, the feedstock fructose price is the next significant parameter which affects the MSP. A 20% change in the fructose price results in a 10.8% change in the MSP for HMF. An inexpensive source of fructose will be necessary to lower HMF price and promote its widescale use. Use of cellulosic sources may reduce the price of fructose, however a detailed study of fructose production from cellulosic sources is essential to determine possible fructose price.

Under the current assumptions, if theoretical yields were achieved from the process, the MSP lowers to \$4.17/gal or \$0.88/kg. This is still a high price to compete with Terephthalic acid through FDCA production at current petroleum prices.

The capital investment for this facility is estimated to be MM\$158 and contributes to 40% of the MSP. There is always an uncertainty surrounding the purchased cost for the equipment. A 20% variation in the purchased equipment cost results in a 8.9% change in the MSP. Better estimates obtained from equipment manufacturers can help reduce the uncertainty in this parameter. The large fraction of capital cost in MSP of HMF, would allow us to take advantage of economies of scale that can be achieved through a larger scale of production. However, since this process is based on a biomass based feedstock, the effect of factors pertaining to economical radius for biomass collection and location of facility should be considered alongwith advantages from economies of scale. Reduction in capital costs for this process through better process design and estimates, will make HMF more attractive by allowing derivatives to compete with petroleum based alternatives.

The price obtained for levulinic acid by-product is also a significant factor affecting the MSP of HMF. With an assumed price of \$300 per MT a 20% variation in this price results in a 1.2% change in the MSP. The current market prices for levulinic acid are higher in the range of \$3210 per MT and at this price, the MSP for HMF reduces significantly to \$0.47 per kg. This process results in a 11000 MT/year production of levulinic acid. This may seem quite high as compared to the 900 MT/year (1999) worldwide demand for levulinic acid. However, levulinic acid can be used as a precursor for a range of chemicals and its market has been expanding every year. Also its production is expanding based on the Biofine technology plants. This increase in production and demand can lead to lower prices for levulinic acid if it is established as a biobased commodity chemical.

DMF production

Simulated mass balance for DMF production process is shown in Table 3.3. The process uses 300 MT/day of pure fructose and 5.57 MT/day of hydrogen as feedstock. Additional makeup chemicals are HCl (used as catalyst), NaCl (applied to enhance HMF partitioning between aqueous and organic solvent phases) and butanol (added to extract HMF from aqueous phase in the CSTR). The product and byproduct flow rates are obtained as 96.6

(98% pure) MT/day, 38 (88% pure) MT/day and 50.4 (96% pure) MT/day of DMF, levulinic acid and unidentified byproduct respectively. The recycle streams are not included in the table.

Table 3.3 Feed and product flow rates for DMF production

Feed Stream		Product Stream		
Raw Materials	Flow Rates (MT/day)	Products	Flow Rate (MT/day)	Purity (%)
Fructose	300	DMF	96.6	97.74
Butanol	0.95	Levulinic Acid	38.01	87.77
HCl	3.74	Byproduct	50.38	96.25
Water	557.1			
NaCl	0.40			
H ₂	5.57			

* rawmaterials are assumed 100% pure

The total installed equipment cost and area wise cost breakdown is shown in Table 3.4. Total installed equipment cost for the base case scenario is estimated as MMS\$121.9 (excluding catalyst cost). The most expensive areas are identified as Area 400 (24% of total installed equipment cost) and Area 500 (46% of total installed equipment cost). In Area 400, DMF is purified through a series of distillation columns. In area 500, fructose is recovered and levulinic acid is purified (to a purity of 87.8%) through evaporators and distillation columns. Both of these areas use several condensers and reboilers.

Table 3.4 Installed equipment and catalyst cost for DMF production

Process Sections	Installed equipment cost	Percent installed equipment cost (with and without catalyst)	
	(MMS)	With Catalyst	Without catalyst
HMF production section (Area 100)	1.30	0.82	1.07
Partial separation section (Area 200)	23.61	14.92	19.37
DMF production section (Area 300)	6.49	4.10	5.33
DMF purification section (Area 400)	28.98	18.31	23.78
Fructose-butanol recovery section (Area 500)	56.04	35.41	45.97
Byproduct recovery section (Area 600)	5.46	3.45	4.48
<i>Sub Total</i>	<i>121.88</i>		
Catalyst*	36.39	22.99	
<i>Total</i>	<i>158.27[†]</i>	<i>100</i>	<i>100</i>

* First time investment of catalyst (indexed to 2007\$ value); [†] including catalyst cost;

The process requires a unique Cu-Ru/C catalyst system. The total catalyst cost for 3 reactors configuration is estimated as MM\$36.4/charge which is approximately a third of the total installed equipment cost.

Cost analysis shows that the Minimum Selling Price of DMF for base case scenario is \$7.63/Gal. This is quite high when compared to the current (Sep 2009) gasoline price of \$2.6/Gal (18). However the price of DMF for chemical use is \$40-46/kg (19). The annual DMF production and yield are 9.9 MMGal and 94.2 Gal/MT of fructose respectively. The total capital investment required for the project is estimated to be 189MM\$ or \$19 per annual gallon capacity. It should be noted that this is only for fructose to DMF conversion. This is also high as compared to similar scale corn ethanol plants at \$2.3 per annual gallon capacity or even cellulosic ethanol which is estimated to be \$6.1 per annual gallon capacity (20). The summary of the detailed analysis is shown in Appendix3A.

The major contributors to the MSP for DMF are indicated in the chart below. Fructose feedstock contributes to 47% of the product price, while a significant expense is also incurred in the recovery of raw materials, which include fructose and butanol. The price of catalyst constitutes 6% of the MSP.

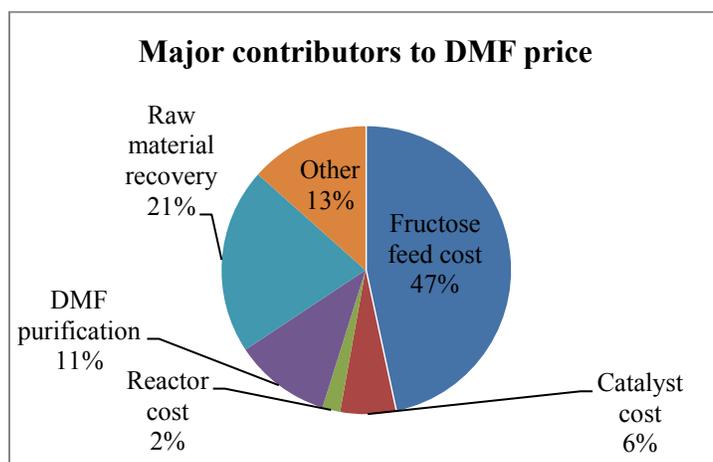


Figure 3.4 Major contributors to DMF price

The process has two major drawbacks: (i) it requires H₂ to convert HMF to DMF. This limits the process to co-locate with excess hydrogen producing plant. If the biorefinery produced excess hydrogen then it would have good utilization in the DMF production

module, otherwise the process would need to generate hydrogen within its battery limit which would require additional capital cost and might increase the MSP of DMF, and (ii) the process uses NaCl to enhance separation of HMF from aqueous phase to organic butanol phase in the biphasic CSTR. NaCl introduces uncertainties in the downstream process performance. Removal of NaCl to significantly low level is cost intensive. It would be interesting to look into alternative organic phase and improved operating conditions that could eliminate NaCl usage.

Sensitivity analysis has been performed on critical process and economic parameters to study their relative significance on MSP of DMF, the parameters and the results are shown in Figure 3.5.

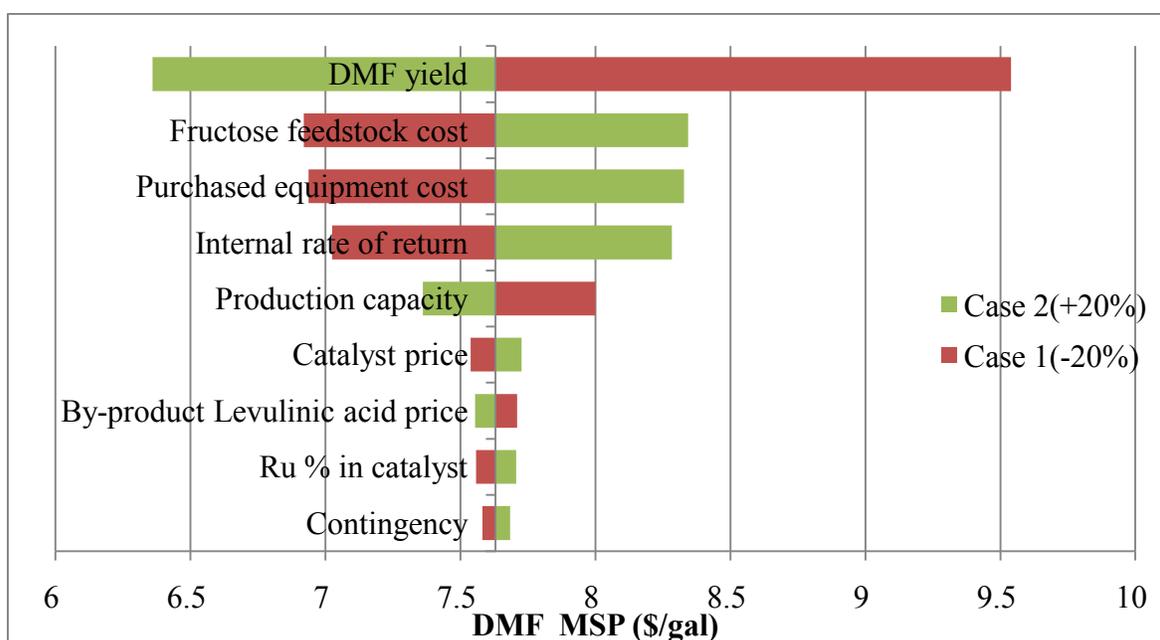


Figure 3.5 Sensitivity analysis on minimum DMF selling price

The yield of DMF from fructose is the most significant parameter affecting the MSP. A 20% increase in the yield can lower the minimum selling price by 16.7%. A part of this yield improvement is required in the HMF production section which has been explained earlier. In laboratory, Dumesic and colleagues (6) obtained DMF yield as 139.9 Gal/MT of fructose. The current process yield (the percentage of process yield to laboratory scale yield)

is calculated as 67%. A net process loss of 4.8 MMGal of DMF per year is observed. This yield loss could be partly due to the application of surrogate chemical properties in the simulation studies, and partly due to reduced effectiveness of the unit operations at larger scale. There are opportunities to minimize these losses through more lab and pilot trials. For economic analysis, if we assume that all of 4.8 MMGal/year of DMF could be recovered then the MSP could be reduced to \$5.14/Gal which would be a substantial cost reduction. Hence, along with lower reactor yields, process loss is a major bottleneck in implementation of this process. The theoretical maximum for this conversion is 156 Gal/MT of fructose which translates to 23.4 MGY of DMF at the assumed scale. If theoretical yields were obtained in the current process, the MSP for DMF reduces to \$3.4/Gal. Following our earlier assumption of 2000 MT/day biomass processing facility, the maximum yield from this conversion will be 14.1 Gal/MT of biomass. This is quite low for fuel use as compared to corn ethanol yield of 105 Gal/MT biomass (20) or even cellulosic ethanol with a yield of 82 Gal/MT biomass (20).

Fructose feedstock cost contributes 47% to the MSP of DMF. A 20% change in the fructose price results in a 9.3% change in the MSP. The large scale availability of inexpensive fructose is a bottleneck for this process, which can be addressed through studies for fructose production from cellulosic sources. In this process 75% of inlet fructose is converted in CSTR and it is assumed that the remaining fructose is recycled after separation from products. However, there is an uncertainty regarding the stability of fructose under the reaction and separation conditions. It is possible that fructose may degrade to other compounds thus further decreasing yields.

Given the high capital costs, the purchased equipment cost has a significant impact on the MSP of DMF. A 20% change in purchased equipment cost results in a 9% change in the MSP. Currently inlet HMF concentration in the PFTR is maintained as 10% w/w (upper limit of the published experimental data) and H₂ fed is 10 times more than the stoichiometric requirement (6). In the simulation, when HMF concentration in the PFTR is doubled from 10 to 20% while keeping H₂ flow unchanged, the MSP reduced to \$7.26/Gal which is a reduction of \$0.37/Gal. It is anticipated that if HMF concentration could be increased further and H₂ flow could be reduced to little over stoichiometric requirements then sizes of the reactor and the purification sections could be reduced significantly which would further

reduce the MSP. Further experiments are needed to test the effects of such changes on yields and catalyst deactivation. The higher capital costs also leave room for significant reductions in MSP by benefiting from economies of scale for higher capacity plants. However, again biomass collection and subsequent plant location will have to be considered in conjunction with economies of scale.

The conversion of HMF to DMF is enabled through use of a Cu-Ru/C catalyst. A 20% change in the price of catalyst results in a 1.2% change in the MSP for DMF. This catalyst is expensive due to the higher percentage of ruthenium. The catalyst contains 8.86% Ru, which is significantly higher than the usual 0.5-1% content of noble metals in catalysts. The use of ruthenium catalyst also has its limitations. Ruthenium is a platinum group metal and is extracted as a product of PGM refining operations. It is a rare metal with limited reserves. Also there many other uses for ruthenium like in the electronics industry which would compete with its use for catalyst. Calculations show that even if 100% of the known ruthenium reserves are diverted to catalyst for DMF production, it can only supply approximately 18% of annual US gasoline consumption(21). Also the catalyst requires frequent regeneration which increases the number of reactors and catalyst requirement for continuous operation. Synthesis of catalysts with longer on-stream times and lower percentage of ruthenium while maintaining or improving performance would certainly reduce the price for DMF. Research into cheaper alternative catalysts is equally important to enable commercial production of DMF.

The levulinic acid by-product can also be a significant factor which affects the MSP of DMF. At the currently assumed price of \$300/MT, a 20% change results in 1% change in the levulinic acid price. However, the price that can be obtained for levulinic acid depends on a variety of factors, which include its purity, current market demand and potential applications.

Conclusion

HMF and DMF production processes appear promising, but this analysis reveals the bottlenecks and uncertainties that need to be overcome for practical implementation. Feedstock availability, lower yields and higher capital costs are the most significant bottlenecks for these processes. Also the use of NaCl to enhance HMF extraction, introduces uncertainties in downstream separation and purification sections.

In case of HMF, increase in yields, inexpensive fructose, lower capital costs and higher price for levulinic acid by-product can lower its price and help establish it as a biobased commodity chemical for a range of other applications.

The process uses expensive CuRu/C catalyst to convert HMF to DMF. The catalyst performance at the present level of development does not seem viable for commercial DMF fuel application. Development of less expensive and effective catalysts with lower rare metal composition is essential for fuel applications. However, the low yields of DMF as compared to other alternative fuels from biomass, can make it unfeasible to pursue DMF solely for fuel applications. To benefit from synergies in a biorefinery it is imperative that new processes be developed which utilize by-products like levulinic acid generated in this process, to produce useful products.

The availability of inexpensive fructose feedstock certainly holds the key to viable large scale production of HMF and DMF and hence it is necessary to develop economically feasible pathways to fructose from biomass. Also this process should be analyzed for its ability to accommodate pure as well as impure glucose feedstock. The use of hydrogen is an important technique in removal of oxygen from biomass compounds. It is essential to investigate renewable sources for hydrogen in a bioeconomy.

These processes could be incorporated as process modules of a bio-refinery. It should be noted that these technologies are still nascent and further technological developments in identified areas can enable practical implementation for chemical applications.

Acknowledgements

We are thankful to The Conoco Phillips Company for the funding that supported this analysis.

Abbreviations

HMF – 5-Hydroxymethyl Furfural

DMF – 2,5-Dimethyl Furan

NaCl – Sodium Chloride

HCl – Hydrochloric acid

FDCA – 2,5-Furan di-carboxylic acid

CSTR – Continuously Stirred Tank Reactor

PFTR – Plug Flow Tubular Reactor

MSP – Minimum Selling Price

MT – Metric Tonnes

Gal – Gallons

MMGal – Million gallons

MM\$ - Million US Dollars

References

1. Aden, A., M. Ruth, K. Ibsen, J. Jechura, K. Neeves, J. Sheehan, B. Wallace, L. Montague, A. Slayton, and J. Lukas. 2002. Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover. NREL report No. NREL/TP-510-32438.
2. Aspen ICARUS. 2006. Aspen Technology Inc., 2006 version. <http://www.aspentech.com>
3. CEPCI, Chemical Engineering Plant Cost Index. 2008. Chemical Engineering, November Issue.
4. Collins, K. 2007. The new world of biofuels: implications for agriculture and energy. EIA Energy Outlook, Modeling, and Data Conference, March 28.
5. Dumesic, J.A., Y.R. Leshkov, and J.N. Chheda. 2008. Catalytic process for producing furan derivatives in a biphasic reactor. US Patent No. 2008/0033188 A1.
6. Durre, P. 2007. Biobutanol: An attractive biofuel. Biotechnology Journal, vol 2, p. 1-10.

7. Johnson Matthey. 2007. Precious metals. <http://www.noble.matthey.com>.
8. Leshkov, Y.R., C.J. Barrett, Z.Y., Liu, and J.A. Dumesic. 2007. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates (including supplementary information). *Nature*, vol. 447, no. 21, p.982-986.
9. Leshkov, Y.R., J.N. Chheda, and J.A. Dumesic. 2006. Phase modifiers promote efficient production of hydroxymethylfurfural from fructose. *Science*, vol. 312, no. 30, p.1933-1937.
10. Perlack, R.D., L.L. Wright, A.F. Turhollow, R.L. Graham, B.J. Stokes, D.C. Erback. 2005. Biomass as feedstock for a bioenergy bioproducts industry: the technical feasibility of a billion ton annual supply. US DOE, contract no. DE-ACO5-000R22725.
11. Peters, M.S., K.D. Timmerhaus, and R.E. West. 2004. Plant design and economics for chemical engineers. McGraw Hill.
12. Qureshi, N. and H.P. Blaschek. 2001. Evaluation of recent advances in butanol fermentation, upstream, and downstream processing. *Bioprocess and Biosystems Engineering*, 24, p-219-226.
13. Qureshi, N. and H.P. Blaschek. 2000. Economics of butanol fermentation using hyperbutanol producing *Clostridium beijerinckii* BA101. *Trans IChemE*, vol 78, Part C, p-139-144.
14. Regalboto, J. R. 2007. Thermochemical conversion of biomass into next generation hydrocarbon biofuels. Growing bioeconomy conference, Iowa State University, Aug 8.
15. Robinson, J.M. 1994. Process for producing hydrocarbon fuels. US Patent No. 5,516,960.
16. Yacobucci, B.D. and R. Schnepf. 2007. CRS report for congress: Selected issues related to an expansion of the renewable fuel standard (RFS). Congressional Research Service, Order Code RL34265.

Appendix 3.A Equipment list and Cost estimates

Table 3.5 Equipment list and installed equipment cost for DMF production

Section	Equipment Number	Number Required	Equipment Name	Installed Equipment Cost 2007 (\$)
Area 100	R-100	1	Biphasic Reactor-CSTR	\$665,725
	M-100	1	Inline Mixer	\$358
	H-101	1	Heat Exchanger	\$278,838
	A100		HMF production	\$944,921
Area 200	D-201	1	Decanter	\$310,672
	D-202	1	Decanter	\$310,672
	D-203	1	Decanter	\$310,672
	D-204	1	Decanter	\$310,672
	D-205	1	Decanter	\$310,672
	D-206	1	Decanter	\$310,672
	H-201	1	Heat Exchanger	\$402,766
	H-202	1	Heat Exchanger	\$173,499
	P-200	1	Pump	\$686,314
	M-201	1	Inline Mixer	\$358
	M-202	1	Inline Mixer	\$358
	A200		HMF separation	\$3,127,326
Area 300	F-300	1	Flash Drum	\$541,003
	R-300	3	Plug Flow Reactor	\$46,467,626
	H-301	1	Heat Exchanger	\$415,158
	H-302	1	Heat Exchanger	\$185,892
	P-300	1	Pump	\$588,269
	M-300	1	Inline Mixer	\$358
	A300		DMF Production	\$48,198,307
Area 400	D-401	1	Distillation column	\$2,416,594
	D-402	1	Distillation column	\$3,061,019
	D-403	1	Distillation column	\$2,230,702
	D-404	1	Distillation column	\$2,255,487
	D-405	1	Distillation column	\$2,658,253
	D-406	1	Distillation column	\$3,061,019

	Equipment Number	Number Required	Equipment Name	Installed Equipment Cost 2007 (\$)
	D-407	1	Distillation column	\$4,907,544
	RB-401	1	Reboiler	\$619,639
	RB-402	1	Reboiler	\$526,694
	RB-403	1	Reboiler	\$433,748
	RB-404	1	Reboiler	\$402,766
	RB-405	1	Reboiler	\$464,730
	RB-406	1	Reboiler	\$322,212
	RB-407	1	Reboiler	\$247,856
	DC-401	1	Column Condenser	\$991,423
	DC-402	1	Column Condenser	\$867,495
	DC-403	1	Column Condenser	\$650,621
	DC-404	1	Column Condenser	\$607,247
	DC-405	1	Column Condenser	\$681,603
	DC-406	1	Column Condenser	\$526,694
	DC-407	1	Column Condenser	\$408,962
	F-400	1	Flash Drum	\$1,552,182
	H-401	1	Heat Exchanger	\$526,694
	H-402	1	Heat Exchanger	\$588,657
	H-403	1	Heat Exchanger	\$433,748
	H-404	1	Heat Exchanger	\$433,748
	H-405	1	Heat Exchanger	\$433,748
	H-406	1	Heat Exchanger	\$433,748
	H-407	1	Heat Exchanger	\$278,838
	H-408	1	Heat Exchanger	\$154,910
	M-400	1	Inline Mixer	\$358
	A400		DMF purification	\$33,178,935
Area 500	D-501	1	Distillation column	\$1,858,918
	D-502	1	Distillation column	\$1,394,189
	D-503	1	Distillation column	\$464,730
	RB-501	1	Reboiler	\$2,974,269
	RB-502	1	Reboiler	\$452,337
	RB-503	1	Reboiler	\$235,463
	DC-501	1	Condenser	\$1,301,243
	DC-502	1	Condenser	\$1,239,279
	DC-503	1	Condenser	\$204,481

	Equipment Number	Number Required	Equipment Name	Installed Equipment Cost 2007 (\$)
	H-501	1	Heat exchanger	\$3,717,836
	H-502	1	Heat exchanger	\$526,694
	H-503	1	Heat exchanger	\$173,499
	A500		Fructose and Butanol Recovery	\$14,542,937
Area 600	D-601	1	Distillation column	\$5,886,574
	D-602	1	Distillation column	\$1,257,868
	RB-601	1	Reboiler	\$681,603
	RB-602	1	Reboiler	\$464,730
	DC-601	1	Condenser	\$1,239,279
	DC-602	1	Condenser	\$681,603
	H-601	1	Heat Exchanger	\$359,391
	H-602	1	Heat Exchanger	\$421,355
	A600		By-product recovery	\$10,992,403
	Total			\$110,984,829

Appendix 3.B Sensitivity parameters and values

Table 3.6 Sensitivity parameters for DMF production

No.	Parameter	Base case		
		Value	Units	MSP
1	No. of PFTR(2:3:4)	3	reactors	\$ 6.70
2	Catalyst cost(1248:1664:2081 \$/kg)	\$1,664.88	\$/kg	\$ 6.70
3	Scenario with no. of PFTR and	3&1664.88		\$ 6.70
4	Catalyst life	2	years	\$ 6.70
5	Original PFTR capital cost(base±25%)	\$349,000	\$	\$ 6.70
6	Contingency(3:10:20%)	3	%	\$ 6.70
7	Levulinic acid price(200:300:600 \$/MT)	\$300.00	\$/MT	\$ 6.70
8	Unknown By-product price(0:50:100)	\$50.00	\$/MT	\$ 6.70
9	Fructose cost(100:300:500 \$/MT)	\$300.00	\$/MT	\$ 6.70
10	DMF Purification Cap. cost (base±25%)	\$10,878,339	\$	\$ 6.70
13	Installation factor(2.5:3:4)	3.05		\$ 6.70
14	Ruthenium % in catalyst(8.86:0.5:1 %)	8.86	%	\$ 6.70
15	Ruthenium price(9.3:18.6:9.3K \$)	18658	\$	\$ 6.70
16	IRR (6:10:20 %)	10	%	\$ 6.70

Appendix 3.C Summary of Process Engineering Analysis

HMF Production

HMF Production Process Engineering Analysis			
HMF Production from fructose			
All Values in 2007\$			
Minimum HMF Selling Price (MHMFSP) : \$5.03 per gallon			
HMF Production (MM Gal. / Year) : 13.0 HMF at 25°C			
HMF Yield (Gal / Tonne Feedstock) : 123.4			
Feedstock Cost \$/MT : \$300			
Internal Rate of Return (After-Tax) : 10%			
Equity Percent of Total Investment : 100%			
Capital Costs		Operating Costs (cents/gal HMF)	
HMF Production	\$1,860,000	Feedstock	243.0
HMF Separation	\$35,370,000	Utilities	26.7
Fructose & Levulinic Acid Recovery	\$65,140,000	Other Raw Materials	8.5
Storage	\$0	Waste Disposal	2.9
Utilities	\$0	Electricity (included in utility cost)	N/A
Total Installed Equipment Cost (TIC)	\$102,370,000	Fixed Costs	38.9
Added Costs (% of TCI)	\$56,020,000 35%	Capital Depreciation	61.1
Total Capital Investment	\$158,390,000	Average Income Tax	40
		Average Return on Investment	81.9
		Operating Costs (\$/yr)	
Installed Equipment Cost/Annual Gallon	\$7.9	Feedstock	\$31,520,000
Total Capital Investment/Annual Gallon	\$12.2	Utilities	\$3,460,000
Loan Rate	N/A	Other Raw Matl. Costs	\$1,100,000
Term (years)	N/A	Waste Disposal	\$370,000
Capital Charge Factor	0.150	Electricity (included in utility cost)	N/A
Maximum Yields (100% of Lab scale)		Fixed Costs	\$5,050,000
Lab scale HMF Production (MM Gal/yr)	14.8	Capital Depreciation	\$7,920,000
Lab scale HMF yield (Gal/ton)	141.1	Average Income Tax	\$5,190,000
Current Process Yield (Model/Lab data)	87%	Average Return on Investment	\$10,630,000
		Major cost contributors	
		Fructose, Levulinic Acid & Butanol Recovery Section (Area 500)	64% of PEC

*Added cost includes startup cost and total indirect plant cost (engineering & supervision, construction expenses, legal expenses, contractor fees and contingency).

DMF Production

DMF Production Process Engineering Analysis			
Fructose Dehydration and HMF hydrogenolysis			
All Values in 2007\$			
Minimum DMF Selling Price (MDMFSP): \$7.63 per gallon			
DMF Production (MM Gal. / Year) :		9.9 DMF at 23°C	
DMF Yield (Gal / Tonne Feedstock) :		94.2	
Feedstock Cost \$/tonne :		\$300	
Internal Rate of Return (After-Tax) :		10%	
Equity Percent of Total Investment :		100%	
Capital Costs		Operating Costs (cents/gal DMF)	
HMF Production	\$1,300,000	Feedstock	318.5
HMF separation	\$23,610,000	Utilities	37.2
DMF Production	\$6,490,000	Other Raw Materials	20.0
DMF Purification	\$28,980,000	Waste Disposal	3.8
Fructose & Butanol recovery	\$56,040,000	Electricity (included in utility cost)	N/A
By-product recovery	\$5,460,000	Fixed Costs	64.8
Total Installed Equipment Cost (TIC)	\$121,890,000	Capital Depreciation	95.3
Added Costs	\$66,690,000	Average Income Tax	65.1
(% of TCI)	35%	Average Return on Investment	158.7
Total Capital Investment	\$188,580,000	Operating Costs (\$/yr)	
Installed Equipment Cost/Annual Gallon	\$12.3	Feedstock	\$31,520,000
Total Capital Investment/Annual Gallon	\$19.1	Utilities	\$120,000
Loan Rate	N/A	Other Raw Matl. Costs	\$1,070,000
Term (years)	N/A	Waste Disposal	\$370,000
Capital Charge Factor	0.167	Electricity	N/A
Maximum Yields (100% of Lab scale)		Fixed Costs	\$6,410,000
DMF Production (MM Gal/yr)	14.7	Capital Depreciation	\$9,430,000
Lab scale DMF yield (Gal/ton)	139.9	Average Income Tax	\$6,440,000
Current Yield (Model/Lab data)	67%	Average Return on Investment	\$15,710,000
		Major cost contributors	
		Fructose, Levulinic Acid & Butanol Recovery Section (Area 500)	46% of PEC

*Added cost includes startup cost and total indirect plant cost (engineering & supervision, construction expenses, legal expenses, contractor fees and contingency).

Chapter 4: General Conclusions

The processes studied here indicate that biomass based renewable chemical processes can potentially provide a sustainable and economically feasible alternative to the current petroleum based processes. We have an extensively developed infrastructure and knowledge base for production and utilization of low oxygen chemical compounds from petroleum sources. Quantitatively as well as qualitatively, it is imperative that we investigate ways to maximize the utilization of existing infrastructure and knowledge base for production of chemical compounds from biomass. This study highlights the challenges faced by chemical catalyst based secondary conversion processes to produce useful low oxygen chemical compounds from biobased platform chemicals. The processes modeled here based on the assumption of a 2000MT/day biorefinery. Techno-economic analysis has given us further knowledge about critical aspects of these processes, like the large scale process yields, capital and operating costs and minimum product value. Sensitivity analysis has allowed us to identify the most important parameters affecting the implementation of these processes and pinpoint areas for further development, which will deliver most bang for the buck. One might argue that this knowledge is subject to assumptions in the study; however until now these processes were developed on the lab scale and little was known about their commercial relevance and feasibility. This study and the assumptions made, open up a black box and reveal useful information about these processes and the use of chemical catalysts in general for biobased conversion.

In the first process, 480MT/day of levulinic acid leads to a production of 194MT/day of Dibutyl Ketone. The process yields are 98% of the lab scale yields and the capital and operating expenses come to around 31.7MM\$ and 538MM\$/year respectively. The process results in production of DBK at a minimum selling price (MSP) of \$8.49 per kg. Higher priced levulinic acid feedstock forms a major fraction of this price. Thus the price of levulinic acid and DBK yield are the most important factors affecting the MSP. Most of the potential for yield increase has to be realized in the reactor, through use of better catalysts and optimum conditions. Levulinic acid can be potentially obtained for a lower value through

the Biofine process. This also indicates that the overall processing cost is low and has a minor effect on the MSP. The value for capital requirement is reasonable for the plant capacity and is in accordance with trend for production of MEK based on iso-butene. Separation or utilization of by-products in a biorefinery can further reduce the MSP of DBK. At \$8.49 per kg, the MSP for DBK is lower than the current price of DBK at \$9 per kg. However, given the potential for widescale use as a solvent, the MSP is quite high as compared to the price of MEK at \$0.77 per kg. Hence, targeting further development in the most critical areas which are identified, will allow DBK to better compete in the market. With low priced levulinic acid from the Biofine process and yields from new technology in lab scale, the MSP for DBK would be in the range of \$0.59 – 0.85 per kg thus enabling it to compete as a commodity scale solvent with MEK. The uncertainties surrounding reactor performance and catalyst behavior can be reduced by further pilot scale studies.

The second process has been modeled to use 300MT/day of fructose feed and results in the production of 174MT/day of HMF at a MSP of \$1.03 per kg and subsequently 97MT/day of DMF at a MSP of \$2.24 per kg. The process yields are 87% and 67% of the lab scale yields for HMF and DMF respectively. The capital expenses and operating costs for only the HMF production are about 158MM\$ and 28MM\$/year. For production of DMF the capital and operating expenses are estimated at 189MM\$ and 40MM\$/year. For fuel applications, the \$7.63 per gallon MSP of DMF, is significantly higher than the current price of gasoline. Also the yields of DMF from biomass are low as compared to corn ethanol and studies for cellulosic ethanol. The capital costs for these processes are also significantly high, and can be a barrier in implementation. Sensitivity analysis shows that the MSP is most sensitive to the process yields and the price of fructose. Even though the MSP for HMF is low, it is comparatively higher to enable widespread applications, as in case of 2,5-furan dicarboxylic acid production. Targeted development towards increasing HMF yields through enhanced reaction yields and prevention of HMF degradation can help lower the MSP. It will also lead to lower capital costs due to reduced purification requirements. In case of DMF, increasing process yields can make it an attractive source for production of numerous furan

derivatives. Given the high MSP and comparatively lower yields on biomass basis, it may not be possible to use DMF as a fuel.

Both the processes seem suitable for chemical applications, and can be important sources for furans and ketones in future. However, further development is needed to overcome bottlenecks, remove process uncertainties and increase efficiencies. Incorporation of these processes as modules in a biorefinery should be considered. Fuel applications do not seem to be feasible at this stage. Significant process development is necessary for fuel production using catalytic process. The major areas of focus for chemical catalyst based technologies are as follows:

Catalysts and Yields: It is essential to develop catalysts, which give high yields and high product selectivity. This will be even more important for chemical applications. For fuel purposes, catalysts producing a range of compounds with potential fuel applications can be quite useful. For fuel applications, it is essential to target compounds with superior fuel properties and a high enough theoretical yield. Also development of catalysts should focus on minimizing the use of rare metals, so as to enable production in large quantities without the uncertainty in supply of rare metals. In the absence of high yields and selectivity, significant separation problems can be expected which result in higher capital costs, operating costs and process uncertainty. Higher capital costs can be a crucial hindrance in implementation of such processes.

Feedstock: Further development is needed for inexpensive and large scale production of biobased starting compounds like glucose, fructose, levulinic acid, etc. It will be a key factor in adoption of biobased chemical and fuel production on a wide enough scale to replace petroleum feedstocks.

These challenges can be overcome with further advances in catalysts and process technology. Catalytic chemical pathway will certainly provide a quicker and viable route for

large scale utilization of biomass resources to produce chemical compounds which are essential to meet our fuel and chemical demands.

Our target here is to produce low oxygen chemical compounds from biomass. Dehydration and decarboxylation, both are useful techniques in removal of oxygen. However the effectiveness of each would be dependent on the price and availability of hydrogen and the biomass source. The desired product could also influence the choice of a strategy. Depending on the number of carbon atoms desired in the product and present in the raw material, individual technique or a combination may be an optimal pathway.

These two processes also provide examples of synergies that can be achieved in a biorefinery. The levulinic acid which is produced as a by-product from the fructose to HMF or DMF process, can be utilized as an input for the production of DBK and other valuable by-products. Economic integration based on production scale and price shows that if levulinic acid at \$300/MT were to be used for production of pure DBK, it results in a \$2.35 per kg MSP for DBK. Such synergies will definitely help improve the efficiency of biomass utilization and increase competitiveness of biobased products against petroleum based products.

Amid the environmental, geo-political, and volatility risks associated with petroleum, use of biomass provides a suitable alternative to reduce our dependence on petroleum, without significantly impacting our quality of life. With the depletion of petroleum sources, biomass based production will certainly make more economic sense. As with every new undertaking, significant innovation and development are needed over time to make the process more efficient. The current efficiency in utilization of petroleum has been achieved through technological innovation, infrastructure development and knowledge gained over the past century. As we move towards developing the bioeconomy, such chemical catalyst based processes will enable us to build upon the knowledge gained and utilize the current infrastructure developed in petroleum economy. This approach which takes advantage of synergies and minimizes losses will enable a quicker and smooth transition to a biobased economy.

Future Work

To compare the effectiveness of either approach, it will be useful to compare biological and chemical pathways for similar products and starting materials.

Evaluation of oxygen removal techniques for similar compounds will provide an insight into the merits and drawbacks, allow us to compare the approaches.

Significant further developments are necessary to realize an efficient biorefinery. More work is needed in developing models for many such individual processes and integrate them to study benefits of potential synergies. Optimization studies should be carried out to select the optimum network of process pathways. This process optimization should be carried out in conjunction with systemwide optimization, so as to minimize waste and increase efficient utilization of biomass resources from the farm to the market for finished products.

Acknowledgements

I am grateful to Dr. Rob Anex for his encouragement, guidance and support throughout my MS studies. My interactions with him have enlightened me and helped develop a new line of thinking and adopt efficient approaches to solving problems. His valuable suggestions have enabled the completion of this thesis.

I am thankful to Dr. Feroz Kabir for his cooperation and guidance which has been instrumental in the completion of a part of this research.

I thank Dr. Raj Raman and Dr. Brent Shanks who took time from their busy schedules to be on my committee. Their valuable suggestions have added to the quality of this document.

I express my gratitude to The Conoco Phillips Company and NSF Engineering Research Center for Biorenewable Chemicals, for funding this research.

Lastly, I would like to thank all those who have supported me in any respect through the completion of my MS studies.