# Phase I Technical Report

## IMPROVED METHOD FOR THE PRODUCTION OF TETRAHYDROFURAN FROM BIOMASS

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## Identification and Significance of the Opportunity and Approach

The overall goal of this Small Business Innovation Research (SBIR) Phase I Project was to demonstrate the technical and economic feasibility of an innovative technology using catalytic reactive distillation and process intensification to manufacture THF from biomass, termed the Intensified Catalytic and Reactive Distillation (iCARD) Process. In the Phase I program, the preferred biomass source for this technology was concluded to be pulp mill waste hydrolysate. The commercially produced tetrahydrofuran (THF) will be used as a replacement for petroleum-derived raw materials in the manufacture of "green" consumer products, including the large volume polyurethane stretch fibers (Spandex), other elastomers, solvents, pharmaceuticals, and coatings.

Based on the results of this Phase I SBIR project, the low manufacturing cost of THF from biomass using the iCARD technology will likely reduce the manufacturing cost of "green" THF sufficiently that conventional production of THF from petroleum will no longer be economic. Current THF production processes require petroleum-based raw materials and significant energy inputs, representing inefficient use of petroleum resources and placing the U.S. at a manufacturing disadvantage compared to chemical manufacturers in Asia. As a result of the economic advantage in the manufacture of "green" THF, the iCARD technology has the potential to be a truly transformational technology for chemicals manufacture from biomass.

Moreover, chemicals produced from petroleum typically are manufactured in billions of pounds annually. Global use of THF for Spandex alone exceeds 1 billion pounds. For biomass sources to be useful for significant displacement of petroleum feedstocks for chemicals manufacture, immense amounts of biomass are required. This requires acquisition and processing of very large quantities of biomass and the separation, purification, sale and/or disposal very large quantities of byproducts.

The pulp and paper industry already processes biomass in very large quantities. A potential source of a biomass for THF production is a waste hydrolysate from the pulp and paper industry. A hot water pre-hydrolysis step, used in many specialty pulp mills, produces a hydrolysate stream which can be readily converted via demonstrated technology to aqueous furfural for THF production. This hydrolysate stream is currently disposed of as waste.

Pulp and paper manufacture is one of the largest industries in the U.S., representing about 6% of the manufacturing sector of the U.S. GDP. In recent decades, the pulp and paper industry has struggled with a declining market, poor profitability, and competition from other world areas, leading to the shutdown of many U.S. pulp and paper mills, and loss of U.S. employment. The production of chemicals, such as THF from pulp and paper waste hydrolysate, can provide new technologies and products from pulp and paper manufacture which can enhance industry profitability. The iCARD technology will produce and sell THF from selected pulp and paper byproduct hydrolysates without deleterious effect on ongoing pulp production of the mill.

THF has been produced on a limited basis from biomass feedstocks in the past, using furfural and furan as key intermediates. However, the conventional technology for converting furfural to THF requires a feed stream of purified furfural. Conversion and recovery of furfural from a dilute biomass hydrolysate as a purified furfural is extremely difficult and energy-intensive, due to the low concentration aqueous solution, the presence of furfural-water azeotropes, byproduct formation in the high temperature distillation, and purification costs. An effective technology for the production of THF from furfural from a dilute hydrolysate stream, without the separation and purification of furfural, is needed. THF is a low boiling compound easily separated from dilute aqueous media, with a favorable azeotrope.

The iCARD technology developed in this SBIR program will take a slip stream of hydrolysate from a hardwood dissolved pulp mill, currently being disposed of through a waste heat boiler at the mill. Hence, the ongoing operations of processing woodchips to pulp will continue, which eliminates much of the burden of a stand-alone chemical production from biomass, including byproducts, low yields, and disposal of waste biomass. The novel KSE technology will take the hydrolysate stream from an existing pulp and paper mill, and return processed hydrolysate to its waste heat boiler. The portion of the hydrolysate stream representing xylan and xylose sugars will be converted to a dilute furfural stream using demonstrated existing mineral acid technology. The dilute furfural stream will then be converted to THF, and potentially other valuable commercial products.

The hydrolysate stream will be converted to furfural, and then to THF, through catalytic reactive distillation of the hydrolysate. Whereas furfural exhibits a boiling point of 162$^oC$, furan has a boiling point of 31$^oC$, and THF has a boiling point of 66$^oC$.[1] Great efficiencies will be achieved by process intensification through catalytic reactive distillation. The furfural is thereby converted into the low boiling point furan and THF, which can be distilled at much greater efficiency, lower cost, and milder conditions.

The proposing firm, KSE, Inc. has conducted catalytic reactive distillation for more than a decade for the formation of ethers, and many other applications. The use of catalytic reactive distillation for reactions in dilute aqueous streams has been successfully demonstrated by KSE, Inc. in ongoing U.S. DOE Phase I, II and III grants[2]. We routinely work with Dr. Michael F. Malone of the University of Massachusetts in reactive distillation technology.[3]

KSE currently retains the services of Dr. Richard Chapas, of Chapas, Chinai and Associates, as an advisor in our commercialization strategy for the iCARD technology, producing "green" THF from pulp mill hydrolysate. Dr. Chapas has served as Vice President of Research and Development at Rayonier, Inc., in Jesup, GA. Rayonier is a global forest products company with more than 85 years of expertise in cellulosic chemistry, and produces hydrolysate suitable for THF production by the iCARD process. This mill regularly develops and implements new technology to improve its profitability.

The new iCARD technology will significantly reduce the energy requirements of THF production from biomass, substantially improve overall process selectivity and process economics, and provide a competitive biobased platform for the production of a large volume commodity chemical. The iCARD technology could potentially be incorporated into cellulosic ethanol plants where acid hydrolysis is used in cellulosic ethanol production, converting its byproduct aqueous stream of furfural[4].

Furfural will be converted to furan directly from the dilute furfural stream in a reactive distillation column. The 31$^oC$ boiling point of furan allows the furan to be rapidly vaporized as it is formed in reactive distillation column, minimizing side reactions due to exposure to the liquid reaction medium. The reactive distillation process uses a "side car" pump-around reactor on the distillation column[5]. Xylan conversion to xylose and furfural will be performed using demonstrated technology.

The overall reaction is shown in simplified form in Equation (1) below.

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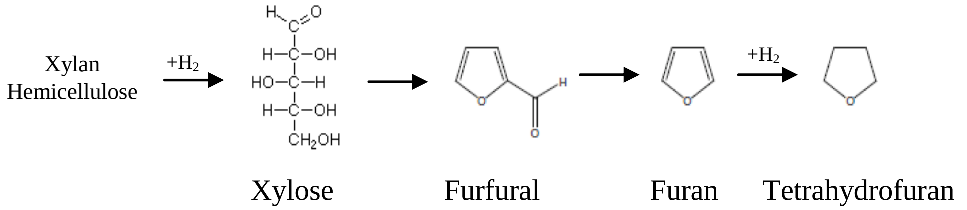
[1] Design considerations include the fact that THF has a 5% azeotrope with water, depending on temperature. Distillation of THF must recognize and avoid the possible explosive formation of peroxides.

[2] Kittrell, J.R. "Reduction of Distillation Usage in the Manufacture of Ethanol by Reactive Water Separation", U.S. DOE Phase I and Phase II SBIR Contracts DE-FG02-08ER85068, June 30, 2008, and Phase III SBIR DE-EE-0004543, October 1, 2010.

[3] See discussions of interactions on reactive distillation with Dr. Malone and Dr. Doherty, at www.kse-online.com.

[4] Sahu, R., Dhepe, P.L., "A one-pot method for the selective conversion of hemicelluloses from crop waste into C5 sugars and fufural by using solid acid catalysts", Chem Sus Chem, Vol. 5, No. 4, 2012, p. 751-761.

[5] Huss, R.S., M.F. Malone and J.R. Kittrell, "Design Methods for Distillation with a Side Car Reactor", Paper 374b, AIChE Annual Meeting, Salt Lake City, November (2007).



(1)

Catalysts were developed in forms that allow them to be installed at specific locations within a reactive distillation column, in addition to the side car reactor, thereby restricting catalytic activity for individual reactions to specific selected locations. Selective catalysts and operating conditions will be used to avoid significant byproduct production of unwanted furfural derivatives. Potential catalyst poisoning by carbon monoxide, a byproduct of furfural decarbonylation, is suppressed.

The Energy Efficiency and Renewable Energy Program of the U.S. Department of Energy identified THF as a high value chemical for potential production from biomass-based feedstocks. The DOE identified the technical barriers to the large scale production of THF from biomass being catalyst tolerance, process operation conditions and reaction selectivity[6]. The novel KSE technology successfully addresses and overcomes all three of these technical barriers.

## Anticipated Public Benefits

Historically, basic chemical intermediates and building blocks have been produced from hydrocarbon feedstocks. The continued reliance on hydrocarbon resources for the production of chemical products is likely unsustainable. Production of basic chemical intermediates from renewable biomass feedstocks will reduce consumption of scarce hydrocarbon resources, and favor installation and employment in the U.S. chemical industry, reversing the trend of locating chemical production in Asia.

The use of an existing hydrolysate stream to produce THF is extremely valuable. The cost of buying, transporting, and processing hardwood chips is already borne by the pulp mill, as they make premium valued pulp product from this operation. Taking a small fraction of this raw material stream to produce THF leaves all the other waste to be burned in the waste heat boiler, as is done if the iCARD process were not installed. This concept provides an extremely attractive basis for producing “green” THF in very large quantities, as a slip steam from the major biomass use for the pulp mill.

In current pulp and paper operations, the Kraft pre-hydrolysis hydrolysate stream is combined with black liquor, concentrated, and then burned. Priced according to fuel value, the value of the xylose in the hydrolysate would be in the range of 3 to 12 cents per pound, depending upon the comparative fuel source. With the proposed KSE iCARD technology, we remove only the furfural product from acid hydrolysis of the entire hydrolysate stream. For example, coproduced acetic acid is rejected from the bottom of the reactive distillation column in the spent hydrolysis stream sent to the waste heat boilers and ethanol byproduct is converted to ethane and used in the waste heat boiler. All other constituents beyond the xylose (converted to furfural) are burned, as is done now with all the Kraft hydrolysate. Little addition byproduct disposal costs should be incurred.

For comparison to the 3 to 12 cent raw material value, with the fuel value basis, THF is currently priced at about \$1.70 per pound. THF is currently produced from maleic anhydride, among other petroleum raw material. Maleic anhydride is currently priced at about \$1.00 per pound[7]. If the price to KSE of hydrolysate from the pulp mill is set at the fuel value of xylose consumed <u>PLUS</u> 20% of the net profits from the iCARD technology operation in the plant, then the manufacturing cost of “green” THF is

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[6] “Top Value Added Chemicals from Biomass, Volume I – Results of Screening for Potential Candidates from Sugars and Synthesis Gas ”, National Renewable Energy Laboratory, U.S. Department of Energy, available at; http://www1.eere.energy.gov/biomass/pdfs/35523.pdfhttp://www1.eere.energy.gov/biomass/pdfs/35523.pdf

[7] “Maleic Anhydride Price Report”, ICIS Chemical Pricing Information, April 10, 2012; http://www.icispricing.com/il_shared/Samples/SubPage171.asp

70 cents per pound. Note that this manufacturing cost of "green" THF is substantially below the raw material cost alone of THF from petroleum sources. A successful commercialization of the iCARD technology will create a transformational change in the manufacture of THF, greatly reducing market prices of THF, and replacing petroleum as the raw material for a global commodity chemical.

The global market for THF is projected to exceed 800 thousand tons by 2017 with growth in THF consumption through 2014 estimated to be 3.8% in the U.S. and as much as 12% in China[8]. Over the past decade the price of THF has increased by 45%, largely driven by increased petroleum raw material costs[9]. The transformation of the THF industry by the iCARD technology will permanently alter these price trends.

Pulp and paper manufacture is one of the largest industries in the U.S., representing about 6% of the manufacturing sector of the U.S. GDP, with over $200 billion in annual sales. The industry employs over one million people, with a total annual payroll of $54 billion[10]. A number of global factors, including the shift to digital media, have resulted in the U.S. pulp and paper market declining at about 1% per year. This overall market decline, coupled with increasing import competition, has resulted in the closure of 177 North American pulp and paper mills over the last 20 years[11]. Faced with such economic pressures, pulp and paper companies are seeking technology and product diversification, with high value products.

The proposed technology will benefit the industry, since pulping routinely separates wood into its hemicellulose, lignin, and cellulose components[12]. Many pulp and paper mills currently utilize a process termed "Kraft pre-hydrolysis", which extracts wood chips with hot water prior to intensive digestion[13]. The resulting hydrolysate stream from hard wood chips consists of a dilute solution of 5-carbon xylan hemicellulose and xylose sugars[14], which are readily converted to furfural[15], and represent an ideal base raw material for production of THF and related compounds. Currently, this stream is concentrated by water removal, and burned[16]. The use of an existing pulp hydrolysate will enable the proposed technology to be economically and commercially used for production THF.

As an example, the dissolved pump mill operated by Rayonier, Inc., in Jesup, GA can produce over 15,000 metric tons per annum (MTPA) of THF, from the iCARD technology. The total U.S. market for THF is now about 150,000 MTPA. Hence, the hydrolysate of one pulp mill of the Rayonier size can supply about 10% of the U.S. market for THF. There are more than a dozen dissolved pulp plants near the Rayonier size in North America. As a transformational technology, the iCARD technology could, in theory, supply the entire U.S. market for THF from the hydrolysate of dissolved pulp mills.

## PRODUCT AND PROCESS FROM PHASE II RESEARCH AND LIKELIHOOD OF COMMERCIAL SUCCESS

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[8] Global Industry Analysts, "Growth in Global Tetrahydrofuran Market Prodded by Opportunities in Biobased Green Manufacturing Technologies, According to a New Report by Global Industry Analysts, Inc." available at: http://www.strategyr.com/Tetrahydrofuran_Market_Report.asp

[9] Global Industry Analysts, "Growth in Global Tetrahydrofuran Market Prodded by Opportunities in Biobased Green Manufacturing Technologies, According to a New Report by Global Industry Analysts, Inc." available at: http://www.strategyr.com/Tetrahydrofuran_Market_Report.asp

[10] Pryke, D.C., "Perspectives on the Pulp and Paper Industry", Alliance for Environmental Technology, 2010; http://www.documents.dgs.ca.gov/pd/epp/PaperForum/PulpandPaper.pdf

[11] "Paper Business Facts", Center for Paper Business and Industry Studies, 2007; http://www.paperstudies.org/resources/industryfacts/today.htm

[12] "Biofuels Feedstocks and Production", Biological and Ecological Engineering Dept., Oregon State University; http://stl.bee.oregonstate.edu/courses/BFP/Class_Slides_W2011/BFP_Lecture6.pdf

[13] "Continuous Pre-hydolysis Kraft Cooking", Continuous Pulping Processes, TAPPI; http://www.sugarresearch.library.qut.edu.au/114/1/Continuous_Pulping_Processes.pdf

[14] Heiningen, A., "Integrated Forest Product Refinery", Final Report, DOE FC36-04GO14306, May 29, 2010

[15] Zeitsch, K.J., "The Chemistry and Technology of Furfural and Its Many By-Products", Elsevier Scienec B.V., Amsterdam, pages 1-74, 2000

[16] "Continuous Pre-hydolysis Kraft Cooking", Continuous Pulping Processes, TAPPI; http://www.sugarresearch.library.qut.edu.au/114/1/Continuous_Pulping_Processes.pdf

## The Product and Technology

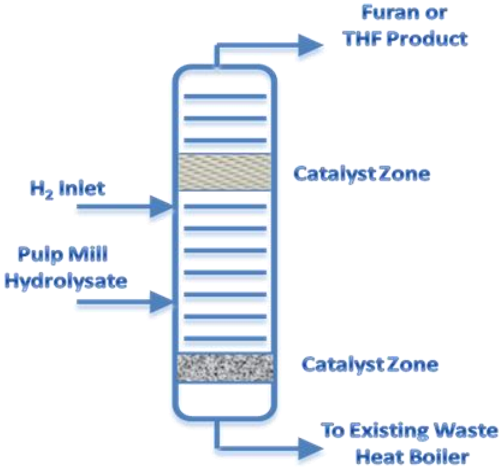
The novel iCARD technology resulting from the Phase II research program will be a commercial process for the manufacture of THF from a hydrolysate stream from cellulose pulp manufacture with exceptionally high selectivity. The process utilizes new decarbonylation and hydrogenation catalysts and novel, highly intensified process technology. The high selectivity minimizes the generation of byproducts, thereby minimizing required separation steps and waste disposal.

In the iCARD technology, production of furan and THF is achieved through the development of novel catalysts, specifically designed for use in reactive distillation columns. The composition and structure of these catalysts will combine the catalytic functionalities to drive the reactions for; (1) hydrolysis of xylan and dehydration of xylose to furfural in the hydrolysate stream, (2) selective decarbonylation of furfural to furan and related products, and (3) selective catalytic hydrogenation to THF and related products. .

In the iCARD technology, process intensification allows xylose to first be converted to furfural/furan directly from the hydrolysate in a reactive distillation column. The furfural/furan will be rapidly vaporized as it is formed, and removed from exposure to high temperature in the distillation pot. Furan side reactions due to exposure to the reaction medium will be minimized. The conversion to THF is performed in a pump-around reactor[17], on the side column.

Figure 1 shows the KSE iCARD reaction as a simple process flow diagram. In this column, furfural is decarbonylated to furan and hydrogenated THF in the reactive distillation column using a side-car reactor. Furfural is formed, converted to furan, and rapidly vaporized as it is formed and removed from exposure to the catalyst. The THF is formed in the side-car reactor, after removing a low-water content furfural/furan slip-stream from the column, hydrogenating it, and returning the reactor products to the column for separation.[18]

**1. Schematic Drawing of Production of THF using KSE iCARD Technology**



The use of biomass based THF will be driven by the increasingly attractive economics of production of large volume commodity chemicals from biomass resources. THF is currently produced from hydrocarbon feedstocks by an extremely lengthy, complex, and energy intensive manufacturing chain. As global population, modernization, and energy demand continue to increase, the cost of hydrocarbon raw materials will continue to escalate, especially for high carbon number products such as THF, unlike the

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[17] Huss, R.S., M.F. Malone and J.R. Kittrell, "Design Methods for Distillation with a Side Car Reactor", Paper 374b, AIChE Annual Meeting, Salt Lake City, November (2007).

[18] Dr. Kittrell holds approximately 25 patents on hydrogen processing catalysts and technologies.

plentiful availability of new U.S. natural gas production and reserves. The use of low cost biomass raw materials, such as waste pulp mill hydrolysate, will provide a basis for the production of THF with extremely attractive manufacturing economics and commercial pricing.

The adoption of biomass based THF will also be driven by increasing societal concern for the environmental impact of many hydrocarbon solvents. Based on current manufacture from hydrocarbon resources, THF is rated poorly in life cycle and environmental impact assessments, largely due to its extremely complex and energy intensive manufacturing chain[19]. Production of THF from pulp mill hydrolysate by the highly intensified iCARD technology will produce THF with a far more attractive life cycle and environmental impact profile.

Based on the process design and economic study completed as part of the Phase I program, the iCARD technology for THF production will provide exceptionally attractive economics, with an estimated payout time of less than 6 months. The iCARD technology is a transformational technology, and will enjoy great commercial success.

The new KSE technology produces THF at a high selectivity and without pre-purification of the dilute furfural. This new technology greatly simplifies purification requirements, reduces waste, and reduces manufacturing cost. The global market for THF is projected to exceed 1.6 billion pounds by 2017, with domestic THF consumption at 320 million pounds. Growth in THF consumption through 2014 is estimated to approach 4% in the U.S. and as much as 12% in China.

The commercially produced THF is designed to provide a low cost route to the production of safe, bio-based polytetramethylene ether glycol (PTMEG) for the production of spandex fibers for use in apparel, hosiery, and other elastomers, which find application in items such as tires, hoses and tubing. The global Spandex market alone is worth $6.8 billion annually.

The demand for THF is currently met by the use of petroleum feedstocks. KSE's innovative technologies allow for the production of THF using our renewable resources, specifically from furfural produced from the hydrolysis of biomass feedstocks, such as corn cobs, wood chips, rice hulls and other plant matter. The use of biomass feedstocks enhances the U.S. industrial base, and provides U.S. employment for the manufacture of a green replacement for hydrocarbon based PTMEG. The biomass replacement of hydrocarbon lessens our dependence on foreign oil, reduces greenhouse gas emissions, and provides a renewable, sustainable, bio-mass based chemical industry.

### Novel Catalysts with Exceptional Activity and Selectivity

Reactions of biomass-derived chemicals are greatly complicated by the many constituents of the biomass broth, which interfere with the separation of furfural. Further, degradation products cause loss of valuable furfural products. New catalysts must be designed to function in these conditions, specifically designed for use in reactive distillation columns.

The Phase I program has successfully demonstrated new catalysts with exceptional activity and selectivity for the production of THF from dilute aqueous furfural. These catalysts are capable of producing THF from dilute water-furfural streams with catalytic activity 3 orders of magnitude greater than conventional catalysts, and with THF yield approaching 100%. These catalysts have been developed in forms specifically designed for use in reactive distillation.

### Reactive Distillation

In many cases, the formation of products of a reaction interferes with the efficiency of the reaction itself. Reactive distillation circumvents these limitations by distilling and removing the interfering reaction species as they are formed. Commercial applications for this technology exist in many

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[19] Capello, C., et al., "What is a Green Solvent? A Comprehensive Framework for the Environmental Assessment of Solvents", Green Chemistry, Vol. 9, pages 927-934, 2007

industrial chemical manufacturing operations. Using its expertise in catalysis, KSE develops highly effective catalysts, specifically tailored for use in reactive distillation columns.

For the conversion of furfural to THF, removing furfural from the reaction mixture as it forms provides higher yields of the furfural. Catalysts that are located higher in the column are used to convert furfural to furan, which alters the azeotrope compositions and improves separation efficiency. The use of reactive distillation minimizes known furfural side reactions, allowing exceptionally high yields to be achieved. The use of reactive distillation also greatly reduces both the cost of furfural purification, required in conventional technology, and post-reaction separation and purification steps.

Low Cost Route to Biomass Based Chemicals

Large scale commercial production of THF will be achieved using the iCARD reactive distillation technology using contained in a pulp mill hydrolysate stream that is currently disposed of as waste. Furfural from pulp mill hydrolysate represents a highly attractive raw material having a substantial price differential with conventional THF manufacture feedstocks.

The key Features, Advantages, and Benefits of the KSE iCARD technology for the production of THF from furfural are summarized in Table 1 below.

**Table 1**
**FAB Matrix for iCARD THF Technology**
**(Features, Advantages, and Benefits)**

| Feature | Conventional Petroleum Based Tetrahydrofuran | KSE, Inc. Biomass Based Tetrahydrofuran |
|---|---|---|
| **Green Product** | **No** | **Yes** |
| **General Purpose Performance Equal to Petroleum Based THF** | n/a | **Yes** |
| **Raw Material Base** | **Petroleum**<br>Hydrocarbon; Oil | **Biomass** |
| **Life Cycle Environmental Impact** | **Severe Impact**:<br>Petroleum Raw Materials,<br>Byproducts,<br>Greenhouse Gas | **Low:**<br>Green Raw Materials,<br>Few Byproducts,<br>Low Energy Usage |
| **Intellectual Property** | **No** | **Yes** |
| **Plant Size Needed for Economic Operations** | **Very Large** | **Small to Large** |
| **Cost** | **High** | **Low** |
| **Transformational Technology** | **No** | **Yes** |

## Likelihood of Commercial Success

KSE will initially commercialize the new technology for the production of biomass-based THF for sale as a “green” THF industrial solvent, and for use in specialty resins and polyols. KSE has a commitment from Optima Chemical for out-sourced production for up to 3 million pounds per year with modest investment. Initial production will be based on furfural sourced from the most competitive priced suppliers based in Asia, demonstrating commercial process performance and catalyst life exceeding one year. Potential customers for initial sales have been identified for THF to qualify the product for commercial use.

After successful commercialization for use as an industrial solvent and for specialty polyols and resins has proven the KSE technology at commercial scale, the pulp mill technology will be installed, to produce THF for production of poly (tetramethylene ether glycol) for production of Spandex fibers. For large scale commercial production of THF for Spandex, furfural will be produced within the reactive distillation process near a dissolved pulp mill, utilizing biomass components contained in a pulp mill hydrolysate stream that is currently disposed of as waste.

The likelihood of commercial success is very high due to: (1) strong market driving forces for use of a biomass based THF product, and (2) highly attractive economics provided by the low raw material costs and the exceptionally high selectivity and efficiency of the novel KSE technology.

The THF selling price, of $1.70 per pound, was taken from the current market pricing information[20]. A summary of the manufacturing costs to produce THF are shown in Table 2, expressed in dollars per pound of THF. The 32 MM lb./yr. case of Table 2 represents a new plant investment at a pulp mill. The commercial plant is planned to be located at the site of a major specialty pulp manufacturer, and will utilize a waste pulp hydrolysate stream as the primary feedstock. The manufacturing cost is the sum of the raw materials cost (adjusted for yield losses), the operating costs, and a capital charge that represents 25% of the capital investment per year. A profit share of 20% is set aside for the pulp mill. The payout time is also shown, at less than 6 months. Note that the manufacturing cost of THF is about 70 ¢/lb, less than the $1/lb price of maleic anhydride[21], the raw material used to manufacture THF today, based on petroleum sources. There are world-scale amounts of hydrolysate in pulp plants compared to THF demand. The iCARD process will likely create a transformation of the commercial methods for producing THF.

**Table 2. Manufacturing Cost of THF with KSE iCARD Technology**

| **Plant Capacity: Pounds THF per year** | **Pulp Plant Case 32 Million lb./yr** |
|---|---|
| **Fixed Capital Investment (USD)** | **$7,965,460** |
| **Capital Charge Rate** | **25%** |
| **Capital Charges (Per lb. THF)** | **$ 0.062** |
| **Total Raw Materials Cost (Per lb. THF)** | **$ 0.168** |
| **Total Process Operating Costs (Per lb. THF)** | **$ 0.187** |
| **Profit Sharing with Pulp Mill (20% of Total Profit)** | **$ 0.269** |
| **Manufacturing Cost of THF (Per lb. THF)** | **$ 0.686** |
| **THF Sales Price (USD/lb)** | **$ 1.700** |
| **Investment Payout Period (Years)** | **0.23** |

Based on the results of Table 1, this Phase I project represents an outstanding financial investment opportunity. The technical and economic feasibility of the iCARD technology has been established.

The use of biomass based THF will be driven by the increasingly attractive economics of production of large volume commodity chemicals from biomass resources. THF is currently produced from hydrocarbon feedstocks by an extremely lengthy, complex, and energy intensive manufacturing chain. As global population, modernization, and energy demand continue to increase, the cost of hydrocarbon raw materials will continue to escalate, especially for high carbon number products such as THF which do not enjoy the plentiful availability of new U.S. natural gas production and reserves. The use of low cost raw materials, such as waste pulp mill hydrolysate, will provide a basis for the production of THF with extremely attractive manufacturing economics and commercial pricing. As the cost of hydrocarbons

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[20] "Adipic Acid& BDO-RHF-PTMEG Market, Weekly Overview", June 14, 2103; *www.pudaily.com/*

[21] "Maleic Anhydride Price Report", ICIS Chemical Pricing Information, April 10, 2012; http://www.icispricing.com/il_shared/Samples/SubPage171.asp

feedstocks continues to escalate, and the production of carbohydrates from lignocellulosic biomass continues to grow, this enormous advantage in basic raw material costs will only increase.

The adoption of biomass based THF will also be driven by increasing societal concern for the environmental impact of many hydrocarbon solvents. Based on current manufacture from hydrocarbon resources, THF is rated poorly in life cycle and environmental impact assessments, largely due to its extremely complex and energy intensive manufacturing chain[22]. Production of THF from pulp mill hydrolysate by the highly intensified KSE technology will produce THF with a far more attractive life cycle and environmental impact profile.

Based on the process design and economic study completed as part of the Phase I program, the KSE technology for FDCA production will provide exceptionally attractive economics, with an estimated payout time of less than 1 year for the first plant. Low raw material costs are an important component of the overall economics. As the cost of hydrocarbons feedstocks continues to escalate, and the production of carbohydrates from lignocellulosic biomass continues to grow, the enormous advantage in basic raw material costs will only increase.

## Phase I Technical Objectives and Approach

The goal of the Phase I SBIR project was to establish the technical and economic feasibility of an innovative catalytic decarbonylation and hydrogenation technology to produce THF by catalytic reactive distillation of dilute aqueous solutions containing furfural.

The specific objectives of the Phase I program were as follows:

1) Define catalysts and catalyst compositions to provide exceptionally high reaction activity, selectivity, and stability for the decarbonylation and hydrogenation of furfural in aqueous solutions to THF. Prepare about 15 solid catalysts, to produce catalyst compositions particularly effective for the catalytic decarbonylation and hydrogenation of furfural. The catalysts will be comprised of catalytic metals such as Pt, Pd, Ni, and W. The catalysts may further be promoted with cations such as Fe, Ce, Cs, K, Ca, and La. Selected catalysts have been shown in the literature to be promising, and will also be evaluated for reference to standard catalysts[23]. Catalyst supports may include silica, titania, zirconia, alumina, carbon, and zeolites.
2) Evaluate the reaction kinetics, selectivity, and stability of the catalysts prepared in catalyst screening experiments. Identify and quantify any observed byproducts. Demonstrate the applicability of the catalysts for achieving exceptionally high reaction rates and high selectivity to the desired THF product. Evaluate the best catalysts in operation in a reactive distillation column, to verify operations and provide design data. Identify the preferred direction for Phase II catalyst optimization for selective catalytic decarbonylation and hydrogenation of furfural to THF, and select the best Phase I catalyst.
3) Conduct a conceptual design for the Phase I technology, and estimate the capital cost, the operating cost, and the total energy costs for the overall system. Conduct process economic studies of the capital cost, the operating cost, and the life cycle costs of the novel technology. Evaluate the economic viability of the Phase I technology, along with other features and benefits, and assess the technical and economic feasibility of the novel technology.

### Phase I Technical Demonstration

The Phase I program has successfully completed all of these objectives, and has successfully demonstrated the technical and economic feasibility of the production of THF from a furfural in dilute

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[22] Capello, C., et al., “What is a Green Solvent? A Comprehensive Framework for the Environmental Assessment of Solvents”, Green Chemistry, Vol. 9, pages 927-934, 2007

[23] See, for example, the catalysts of the references of this proposal, and those of Corma, A.; Iborra, S.; Velty, A. Chemical Routes for the Transformation of Biomass into Chemicals. *Chem.Rev.* **2007**, 107, 2411-2502.

aqueous solution with exceptionally high activity and selectivity:

- New catalyst compositions have been developed with catalytic activity for furfural conversion which exceed the activity of conventional catalysts by 2 to 3 orders of magnitude. The feasibility of achieving selectivity to the desired THF product approaching 100% has been demonstrated.
- The Phase I program has demonstrated the ability to produce pure THF, or can be arranged to produce other valuable commercial products such as tetrahydrofurfuryl alcohol, 1,5-pentanediol, 2-methyl furan, and 2-tetrahydromethylfuran as co-products with THF.
- A preliminary design for the Phase I technology has been completed using the Aspen One Process Simulator. Capital costs, operating costs, and energy costs for the overall system have been estimated, as summarized in Table 2.
- A preliminary design for the Phase I technology has been completed using the Aspen One Process Simulator. Capital costs, operating costs, and energy costs for the overall system have been estimated. Based on the use of waste pulp mill hydrolysate as the biomass raw material source, the new technology will produce THF for a total manufacturing cost of about $0.70 per pound, with an investment payout time of less than six months. The manufacturing cost of the "green" THF is less than the raw material cost for the hydrocarbon-based feed stocks for conventional THF production.

## Task 1. CATALYST SYNTHESIS AND FORMULATION

In Task 1, catalysts were synthesized and their properties assessed, in order to develop new catalyst formulations necessary for furfural decarbonylation and hydrogenation to produce THF. In Task 1, over 15 solid catalysts were prepared, to produce catalyst compositions particularly effective for (a) the catalytic decarbonylation of furfural in the presence of hydrogen, and (b) the hydrogenation of furan to THF. Palladium impregnated alumina and charcoal catalyst were prepared, to serve as benchmark catalysts. These two compositions are the most prevalent catalysts sited for furfural decarbonylation in the literature. In addition, the best KSE catalyst compositions were prepared in a form suitable for application to a reactive distillation column, for example, being employed as a reactive coating on distillation column packing.

High catalyst activity is important, to enable use of milder reaction conditions for reduction of side reactions, "polymeric or carbonizing byproducts", and use in reactive distillation. High selectivity (>90%) is paramount, to improve process economics by avoiding loss of valuable product and catalyst deactivation. The catalyst must resist fouling and formation of surface deactivating agents, and retain stable activity and selectivity, over extended run duration in order for the catalyst to be commercially useful. The catalyst must also have robustness to survive the rigors of a reactive distillation column.

The decarbonylation of furfural to furan has been widely described in the literature for both liquid phase and gas phase reactions, using conventional catalysts comprised of palladium and carbon[24,25,26,27,28], and alternatively, palladium and alumina.[29, ,30,31]. Alkali metal promoters, especially cesium carbonate,

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[24] Gaset, A., et al., "Process for the Decarbonylation of Furfural to Produce Furan, EP0096913, December 18, 1983

[25] Gaset, K.J.J.A., Molinier, J., "Furfural Decarbonylation Catalyzed by Charcoal Supported Palladium: Part I- Kinetics.", Biomass 16 (1988) pgs 63-76

[26] Gaset, K.J.J.A., Molinier, J., "Furfural Decarbonylation Catalyzed by Charcoal Supported Palladium: Part II- A Continous Process", Biomass 16 (1988) pgs 89-96

[27] Zeitsch, K.J., "The Chemistry and Technology of Furfural and its Many Byproducts", Elsevier Science, Amsterdam, pages 156-158, 2000

[28] Copelin, H.B., Garnett, D.I "Decarbonylation of Furfural" US Patent 3,007,941 November 7, 1961

[29] Zeitsch, K.J., "The Chemistry and Technology of Furfural and its Many Byproducts", Elsevier Science, Amsterdam, pages 156, 2000

[30] Wambach, L., et al., "Preparation of Furan by Decarbonylation of Furfural", U.S. Patent 4,780,552, October 25,

are commonly used. Gas phase reaction is cited as the preferred reaction mode for minimizing furfural loss to side reactions. In either gas or liquid phase reactions, the process is known to be prone to the formation of "polymeric or carbonizing byproducts", resulting in both poor selectivity to the furan, and catalyst deactivation due to precipitation of the byproduct solids on the surface of the catalyst[32],[33], [34]. The presence of water can also be detrimental to furfural conversion selectivity by driving both polymerization and hydrolysis side reactions[35].

Conversion of furfural to THF by decarbonylation in the presence of hydrogen has also been widely studied. The presence of hydrogen not only allows for hydrogenation of furan to THF, but also suppresses side reactions to oligomeric and polymeric compounds[36,37]. For example, the decarbonylation of furfural to THF has used silica supported metal (Cu, Pd, and Ni) catalysts in the presence of hydrogen at about 200 to 250°C in an aqueous medium. Although 100% furfural conversion was achieved, only 14% yield of THF was accomplished[38,39]. THF has also been produced from furfural with a Zn-Cr-Mo catalyst, followed by hydrogenation[40]. Significant production of byproduct furfuryl alcohol and unsaturated furan were produced, as well as lesser amounts of butanol and butane. The catalyst also hydrogenated the carbonyl group to form furfuryl alcohol. Additionally, the hydrogenation function of the catalysts can destroy the cyclic ether ring during the decarbonylation of the furfural[41],[42].

Simultaneous decarbonylation and hydrogenation in the presence of hydrogen can result in a wide range of potential products[43]. Catalyst composition and structure, along with selection of reaction conditions, may be optimized to target the production of specific compounds. Furfural was hydrogenated to furfural alcohol using palladium dispersed over metal oxide supports. By varying the palladium distribution, palladium particle size, in conjunction with the support, THF, 2-methylfuran, and 2-methyltetrahydrofuran were co-produced[44]. A palladium carbon catalyst produced these products as well, in addition to furan ring opened compounds, 2-pentanone, 2-pentanol and 1 pentanol[45]. A two catalyst system using a combination of copper, chromium, and manganese catalyst followed by a reduced nickel

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1988

[31] Li, K., and Ozer, R., "Vapor Phase Decarbonylation Process", U.S. Patent 8,404,871, March 26, 2013

[32] Li, K., and Ozer, R., "Vapor Phase Decarbonylation Process", U.S. Patent 8,404,871, March 26, 2013

[33] Gaset, K.J.J.A., Molinier, J., "Furfural Decarbonylation Catalyzed by Charcoal Supported Palladium: Part II- A Continuous Process", Biomass 16 (1988) pgs 89-96

[34] Gaset, K.J.J.A., Molinier, J., "Furfural Decarbonylation Catalyzed by Charcoal Supported Palladium: Part I-Kinetics.", Biomass 16 (1988) pgs 63-76

[35] Copelin, H. and Garnett, D.I., "Decarbonylation of Furfural", U.S. Patent 3,007,941, November 7, 1961

[36] Wambach, L., et al., "Preparation of Furan by Decarbonylation of Furfural", U.S. Patent 4,780,552, October 25, 1988

[37] Li, K. and Ozer, R., "Vapor-Phase Decarbonylation Process", U.S. Patent 8,404,871, March 26, 2013

[38] Sitthisa, S., et al., "Conversion to furfural and 2-methylpentanal on Pd/$SiO_2$ and Pd-Cu/$SiO_2$ Catalysts", Journal of Catalysis, Vol. 280, 2011, p. 17-27.

[39] Sitthisa, S., Resasco, D. E., "Hydrodeoxygenation of Furfural Over Supported Metal Catalysts: A Comparative Study of Cu, Pd and Ni", Catalysis Letters, Vol. 141, 2011, p. 784-791.

[40] Wittcoff, H. A.; Reuben, B. G.; Plotkin, J. S., "Industrial Organic Chemicals, Second Edition", John Wiley & Sons: New Jersey, 2004; p 442.

[41] Sitthisa, S., et al., "Selective Conversion of Furfural to Methylfuran Over Silica-Supported Ni-Fe Bimetallic Catalysts", Journal of Catalysis, Vol. 28, pages 90-101, 2011

[42] Wabnitz, T., et al., "Process for One-Stage Preparation of 2-Methyltetrahydrofuran from Furfural Over a Catalyst", U.S. Patent Application 20100099895, April 22, 2010

[43] Zheng, H-Y, et al., "Toward Understanding the Reaction Pathway in Vapor Phase Hydrogenation of Furfural to 2-Methylfuran", Journal of Molecular Catalysis, Vol. 246, pages 18-23, 2006

[44] Sitthisa, S., et al., "Selective Conversion of Furfural to Methylfuran Over Silica-Supported Ni-Fe Bimetallic Catalysts", Journal of Catalysis, Vol. 28, pages 90-101, 2011

[45] Wabnitz, T., et al., "Process for One-Stage Preparation of 2-Methyltetrahydrofuran from Furfural Over a Catalyst", U.S. Patent Application 20100099895, April 22, 2010

catalyst made primarily 2-methylfuran and 2-methyltetrahydrofuran[46,47], while a bi-metallic nickel iron catalyst made 2-methylfuran[48]. Rhodium doped silica and a rhenium/iridium silica catalyst produced 1, 5-pentanediol, [49,50]. Reaction conditions influence the reaction pathways as well, but these examples illustrate the necessity of a catalyst composition which is tailored to a decarbonylation pathway and will allow for hydrogenation to THF without opening the furan ring.

For the hydrogenation catalyst used to hydrogenate furan to THF, ring opening is to be avoided during hydrogenation. This is avoided by using mild hydrogenation conditions and avoiding an acidic character to the catalyst. This can be achieved by modifying catalysts with alkali metals such as potassium, magnesium, and calcium. Choice of silica/alumina ratio in catalyst such as the zeolites can also mitigate the acidity of the catalyst.

Deactivation of the catalyst is also a chief concern. Deactivation of furfural decarbonylation catalysts are well known in literature[51,52,53,54,55]. This deactivation process may be due to the coking of furfural on the catalyst surface, reducing active sites for the decarbonylation reaction, or the blockage of pores by coking, leading to deactivation of the catalyst. A third possibility is the poising of the catalyst by carbon monoxide. Judicious selection of catalyst co-components and carrier material was conducted with this in mind. KSE has already developed a noble metal catalyst for CO oxidation. The characteristics and morphology of the catalyst carrier were considered in mitigating coking effects, and selection of catalytic metal and supports were investigated for prolonging of activity by avoiding CO poisoning.

Several carriers were investigated, including alumina, base modified alumina's, silica, several forms of carbon, titania, zeolites, both ammonium and hydrogen forms, and zirconia. Typical surface areas for these catalysts were in the range of 200-300 $m^2/g$, however, the range for all those tested was 50 to over 1000 $m^2/g$. The zeolite catalysts had varied silica alumina ratios as well as varied levels of retained sodium, to determine the effect of varied acidity on the formation of side reactions. The acidity of a catalyst is known to cause furan ring opening and loss of product yield[56]

Catalysts were modified with metals by impregnation using incipient wetness. Several different metal compositions and metal loading levels were tested. Order of impregnation was also varied. It is known the carrier attributes, such as pore size, pore volume, pore distribution, surface area, and chemical composition will affect the activity and selectivity of a catalyst. These attributes will also affect the metal dispersion on the surface of the catalyst. The choice of metal promoter will also affect activity and

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[46] Ahmed, I., "Process for the Preparation of 2-Methylfuran and 2-Methyltetrahydrofuran", U.S. Patent Application 20030018205, January 23, 2003

[47] Ahmed, I., "Process for the Preparation of 2-Methylfuran and 2-Methyltetrahydrofuran", U.S. patent 6,479,677, November 12, 2002

[48] Sitthisa, S., et al., "Selective Conversion of Furfural to Methylfuran Over Silica-Supported Ni-Fe Bimetallic Catalysts", Journal of Catalysis, Vol. 28, pages 90-101, 2011

[49] Koso, S., et al., "Chemoselective Hydrogenolysis of Tetrahydrofurfuryl Alcohol to 1,5-Pentanediol", Chemical Communication, Royal Society of Chemistry, 2009; http://pubs.rsc.org/en/Content/ArticleLanding/2009/CC/b822942b#!div

[50] Nakagawa, Y. and Tomishige, K., "Production of 1,5-Pentanediol from Biomass via Furfural and Tetrahydrofurfuryl Alcohol", Catalysis Today, Vol. 195, Issue 1, pages 136-143, 2012

[51] Lejemble, P. et al. "From Biomass to Furan Though Decarbonylation of Furfural under Mild Conditions." Biomass 4 (1984) pg 263-274

[52] Li, et al. "Vapor Phase Decarbonylation Process", U.S. Patent 8,404,871 Mar. 26, 2013

[53] Wambach, L. et al. "Preparation of Furan by Decarbonylation of Furfural", US Patent 4,780,552 October 25, 1988

[54] Gaset, K.J.J.A., Molinier, J., "Furfural Decarbonylation Catalyzed by Charcoal Supported Palladium: Part II- A Continuous Process", Biomass 16 (1988) pgs 89-96

[55] Gaset, K.J.J.A., Molinier, J., "Furfural Decarbonylation Catalyzed by Charcoal Supported Palladium: Part I- Kinetics.", Biomass 16 (1988) pgs 63-76

[56] Diebold, J.P, Evans, R.J. Process for Producing Furan from Furfural Aldehyde. US Patent 4,764,627 August 16, 1988

reaction pathways. These variables were identified and considered when preparing catalyst for Task 1 study, and will be more thoroughly investigated in the Phase II program.

The catalyst compositions prepared were initially screened for activity, measuring conversion of furfural at a standard condition. Those with promising reaction kinetics proceeded to a second testing stage, where catalyst selectivity, catalyst longevity, and decarbonylation and hydrogenation characteristics were studied. Furfural can react to a wide variety of different chemicals, and by modification of the catalyst and reaction parameters the selectivity of the catalyst was altered to produce many of these, such as furfural alcohol, tetrahydrofurfuryl alcohol, 2-methylfuran, and 2-methyl tetrahydrofuran, among others (see Figure 3). However, the goal of this Phase I project was to produce a catalyst and system for production of THF, so those catalyst compositions and reactor conditions which exhibited strong decarbonylation pathway selectivity were chosen over others. Table 3 summarizes the categories of catalysts which were tested for furfural reaction activity, with variants on each.

**Table 3**
**Catalyst Compositions Developed and Tested for Reactions**
**C is used to represent various activated carbons, each designated by a subscript**

| Catalyst ID | Zr | $C_1$ | $C_2$ | Al | S | $C_3$ | Ti | Si | Pt | $C_4$ | Pd | Rare Earth | Ni | $C_5$ | Na | O | Ba | K | Ca | Mg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CATJ100 | | | | | x | | | | | | x | | | | | x | x | X | | |
| CATJ107 | | x | | | | | | | X | | | | | | | | | | | |
| CATJ114 | | | | | | x | | | | | x | | | | | | | | | |
| CATJ117 | | | | x | | | | | | | x | | | | | x | | | | |
| CATJ118 | | | x | | | | | | | | x | | | | | | | | | |
| CATJ143 | | | | | | | x | | | | x | | | | | x | | | | |
| CATJ145 | | | | | | | | x | | | | | | | | x | | | | |
| CATJ147 | | | | | | | | x | | | x | | | | | x | | | | |
| CATJ149 | | | | x | | | | x | | | x | x | | | x | x | | | | |
| CATJ151 | | | | x | | | | x | | | x | x | | | x | x | | | | |
| CATJ157 | | | | x | | | | x | | | x | x | | | | x | | | x | x |
| CATJ169 | x | | | | | | | | | | | | | | | | | | | |
| CATJ171B1 | | | | x | | | | x | | | x | x | | | x | x | | | | |
| CATJ171B2 | | | | x | | | | x | | | x | | x | | x | x | | | | |
| CHEMR21W | | | | | | | | | | x | x | | | | | x | | X | | |

Catalyst preparation and evaluation focused on compositions which could be incorporated into physical form and shapes that would be readily used in a reactive distillation column. The forms and shapes selected would perform effectively both as reaction catalysts, and as distillation packing. An example of catalysts prepared for use in a reactive distillation column is shown in Figure1. The saddle and ring shaped catalysts shown in Figure 2 are widely used as distillation packing, and have been coated with THF catalysts of the present program.

**Figure 2**
**Catalyst Forms Used in Reactive Distillation**

## Task 2. LABORATORY STUDIES OF CATALYST PERFORMANCE

The purpose of Task 2 catalyst evaluations was to define catalysts, reaction compositions, and reaction conditions particularly effective for the decarbonylation and hydrogenation of furfural to THF.

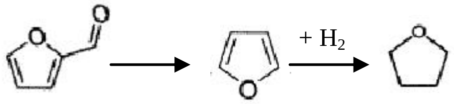
In a simplified view of the novel KSE reactive distillation technology, furfural in dilute aqueous solution is converted to furan and THF in the integrated reactive distillation process. Reactive distillation will allow the volatile furan and THF products to be rapidly removed from the reaction medium, thereby (1) minimizing furfural side reactions, (2) eliminating the separate energy intensive furfural purification from the dilute aqueous solution required by conventional technology, and (3) minimizing post-reaction separation and purification steps required by conventional technology.

Catalyst performance studies provided reactive testing of the prepared catalysts, under realistic reaction conditions anticipated in a reactive distillation environment for decarbonylation and hydrogenation of furfural to THF. These compositions and temperatures selected for Task 2 catalyst testing were selected from iCARD process simulation runs in Task 3, to represent actual conditions in the reactive distillation column. The tests assessed the activity of each prepared catalyst, with extensive evaluation of product selectivity for the highest activity catalysts, and a preliminary assessment of deactivation for the best catalysts. Selectivity is measured as the percentage of the furfural converted to the desired THF product, in the data that follow. First order kinetics models were used for comparative catalyst activity assessments in this Phase I program, to inter-relate effects of space velocity, temperature and conversion, when comparing the activity of various catalysts

To further explain catalyst test conditions, Aspen reactive distillation process simulations were extensively utilized to provide guidance and direction for the catalyst performance studies. The reactive distillation simulations, and process streams taken from the column, provided reaction compositions for both liquid and gas phases, along with ranges for temperature and other reaction conditions for use in the catalyst performance evaluations. The results of the catalyst evaluations were then used to both to guide further catalyst preparations, and to fine tune the reactive distillation simulations. Catalyst preparation and evaluations, and the reactive distillation process configuration that the catalysts would be utilized in, were effectively developed in an iterative integrated process, as described below.

Reaction Chemistry, Pathways, and Products

The overall reaction for the conversion of furfural to THF is shown in simplified form in Equation (2) below.

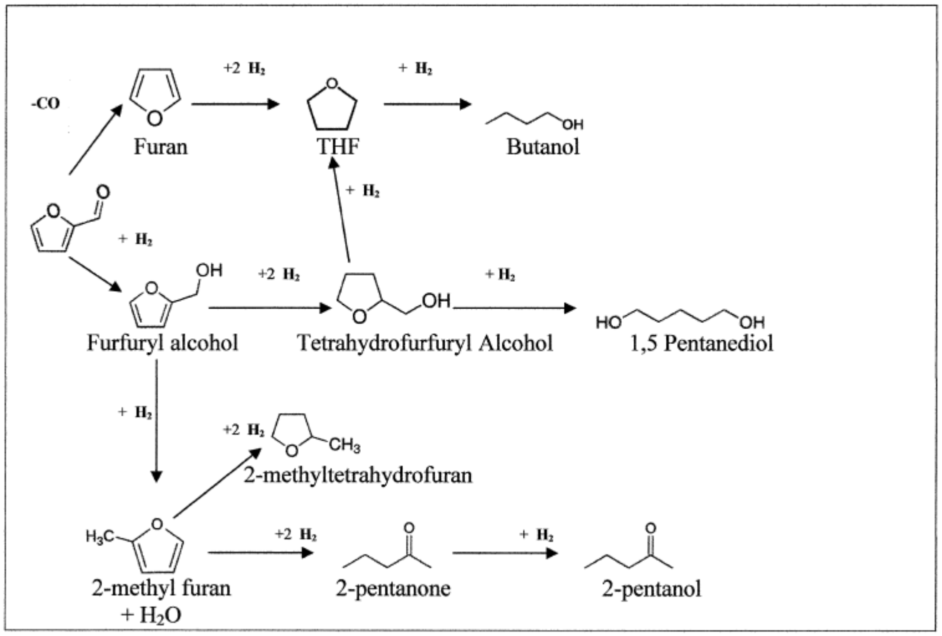


(2)

Furfural is first decarbonylated to form furan, with carbon monoxide (CO) as a byproduct. The furan intermediate is then hydrogenated to produce tetrahydrofuran (THF). Both furan and THF are useful products in the marketplace.

In reality, the production of THF from furfural, especially with decarbonylation and hydrogenation reactions conducted simultaneously, is far more complex than indicated in Equation (2). A more complete depiction of the reaction chemistry and pathways is shown on Figure 3.

**Figure 3[57]**
**Reaction Pathways for the Decarbonylation and Hydrogenation of Furfural**



In the presence of hydrogen, the conversion of furfural into intermediate and final products will proceed along two primary pathways; a decarbonylation pathway and a hydrogenation pathway. Both pathways have multiple sequential reaction products.

In the decarbonylation pathway, the furfural is first decarbonylated to form furan, with CO as a byproduct. The furan is then hydrogenated to THF. Although THF does represent a stable final product, with certain catalysts it may be converted to $C_4$ alcohols by ring opening hydrogenolysis[58].

In the hydrogenation pathway, furfural is first hydrogenated to furfuryl alcohol. The hydrogenation pathway then divides into two secondary pathways. In one pathway, the furfuryl alcohol (FA) is hydrogenated to tetrahydrofurfuryl alcohol (THFA). THFA may then be converted by hydrogenolysis to THF, or by ring opening hydrogenolysis to 1,5-pentanediol[59]. In the other pathway the FA is converted by hydrogenolysis to 2-methyl furan. The 2-methyl furan may then be hydrogenated to 2-methyltetrahydrofuran. 2-Methyl furan may also be converted to $C_5$ aldehydes and alcohols by ring opening hydrogenolysis[60].

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[57] Zheng, H-Y, et al., “Toward Understanding the Reaction Pathway in Vapor Phase Hydrogenation of Furfural to 2-Methylfuran”, Journal of Molecular Catalysis, Vol. 246, pages 18-23, 2006.

[58] Zheng, H-Y, et al., “Toward Understanding the Reaction Pathway in Vapor Phase Hydrogenation of Furfural to 2-Methylfuran”, Journal of Molecular Catalysis, Vol. 246, pages 18-23, 2006

[59] Nakagawa, Y. and Tomishige, K., “Production of 1,5-Pentanediol from Biomass via Furfural and Tetrahydrofurfuryl Alcohol”, Catalysis Today, Vol. 195, Issue 1, pages 136-143, 2012

[60] 60 Zheng, H-Y, et al., “Toward Understanding the Reaction Pathway in Vapor Phase Hydrogenation of Furfural to

Catalyst composition and morphology were selected to catalyze both the decarbonylation and hydrogenation reactions at exceptionally high activity and selectivity to the desired THF product. In order to support the furan hydrogenation reaction step shown in Equation (2), the reaction is conducted with hydrogen as the reaction gas. In addition to supporting the hydrogenation reaction step, hydrogen has been shown to minimize furfural loss due to side reactions[61,62]. Surprisingly, effective performance of the hydrogenation reaction was achieved at mild operating pressure, able to be used in a reactive distillation column.

Although THF was the primary desired product in the Phase I study, it must be noted that THF is not the only commercially significant product among the various reaction products shown in Figure 3. The use of THFA as a biodegradable solvent in commercial uses where solvent are applied directly into the environment, such agrochemical formulations and cleaning applications, is increasing rapidly. THFA is also being evaluated as a solvent in cosmetics, personal products, and paints and other coatings[63]. 2-Methyltetrahydrofuran represents a potential biomass-based "green" alternative to THF for solvent applications where lower water solubility is required[64]. Green solvents will be most attractive for use in cosmetics, toiletries, and other personal products. Regulatory pressures for VOC emissions from paints and coatings continue to mount, providing increasing incentive for replacement of hydrocarbon solvents in paints[65].

2-Methylfuran is used as a fine chemical intermediate for the synthesis of pesticides and a variety of medical and personal products[66]. 1,5-Pentanediol is widely used in epoxy and polyurethane coatings, and a variety of cosmetics and personal products[67].

In addition to high reaction selectivity to THF, the KSE Phase I catalysts can also be further optimized for the production of THFA, or co-production of THF and THFA. Specific KSE Phase I catalysts were also observed to produce amounts of 1,5-pentanediol, 2-methylfuran, or 2-methytetrahydrofuran. The composition and structure of these catalysts will be further examined during the Phase II program for possible optimization to catalysts specifically selective to these products. The production of several commercially valuable products from furfural represents an important commercial opportunity which will be explored further during the Phase II program.

## Reactive Distillation Process Configuration

The reactive distillation process configuration, including catalyst location, along with the physical, chemical, and thermodynamic properties of the system components, determine the composition and reaction conditions under which the catalysts must perform.

As shown schematically in Figure 4, there are two basic process catalyst configuration options for catalytic reactive distillation:

- In-column reaction. In this configuration, the catalyst is directly installed inside the column, either in the form of inorganic packing shapes coated or impregnated with catalytic components, or in the form of a "structured packing" where catalyst materials are retained in a specially

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2-Methylfuran", Journal of Molecular Catalysis, Vol. 246, pages 18-23, 2006

[61] Wambach, L., et al., "Preparation of Furan by Decarbonylation of Furfural", U.S. Patent 4,780,552, October 25, 1988

[62] Li, K. and Ozer, R., "Vapor-Phase Decarbonylation Process", U.S. Patent 8,404,871, March 26, 2013

[63] "THFA; Low Cost Biodegradable Solvent", Pennakem; http://www.pennakem.com/pdfs/THFAgreenTDS120aF1004.pdf

[64] Aul, R. and Comanita, B., "A Green Alternative to THF", May, 2007; http://www.romil.com/me2thf.pdf

[65] "Architectural Coatings Program – VOC limits", http://www.arb.ca.gov/coatings/arch/voclimits.htm

[66] Zheng, H-Y, et al., "Toward Understanding the Reaction Pathway in Vapor Phase Hydrogenation of Furfural to 2-Methylfuran", Journal of Molecular Catalysis, Vol. 246, pages 18-23, 2006

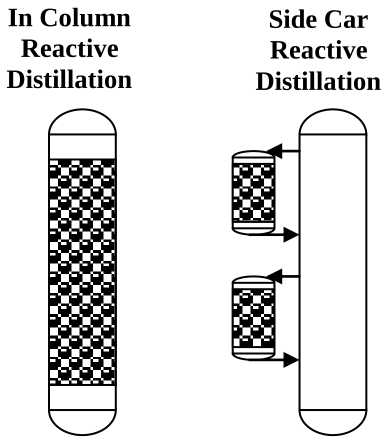
[67] Rector, F.D., "Thermosetting Coating Composition", U.S. Patent 5,288,820, February 22, 1994

designed interior column metal structure[68].

- Side car reaction. In this configuration, the catalyst is installed in one or more separate reaction vessels which are fed by either gas or liquid streams taken from the column, and with the reactor exit streams returning to the column[69]. If the return stream is returned adjacent to the tray from which it is withdrawn, then it is effectively equivalent to a catalyst place on the withdrawal tray inside the column. An advantage of the side-car reactor is greater flexibility on control of catalyst and temperature, that that dictated by the bubble point of a liquid on a column tray.

With an in-column catalyst configuration, the reaction will take place in the liquid phase, vapor phase, or in combined liquid and vapor phases. Reaction conditions are limited to equilibrium conditions within the column. With a side car configuration, reaction conditions within the side car reactor are substantially independent of column equilibrium conditions, and may be conducted in either liquid or gas phase.

**Figure 4**
**Reactive Distillation Catalyst Configuration Options**



A key factor in the selection of the reactive distillation process configuration is the preferred phase, liquid or vapor, for conducting the reaction.

In either gas or liquid phase reaction, furfural decarbonylation is known to be prone to the formation of oligomeric and polymeric byproducts, resulting in both poor selectivity to the furan, and catalyst deactivation due to precipitation of the byproduct solids on the surface of the catalyst[70,71,72]. Although liquid phase furfural decarbonylation processes have been historically reported, literature sources cite gas phase decarbonylation as the preferred route for both catalytic activity and furan selectivity[73,74,75,76]. The

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[68] "Structured Packings", Sulzer Ltd.; http://www.sulzer.co/en/Products-and-Services/Separation-Technology/Structured-Packings

[69] R. S. Huss, M. F. Malone and J. R. Kittrell, " Design Method for Distillation with a Side Car Reactor," paper 374b, AIChE 2007 Annual Meeting, Salt Lake City, November (2007).

[70] Li, K., and Ozer, R., "Vapor Phase Decarbonylation Process", U.S. Patent 8,404,871, March 26, 2013

[71] Gaset, K.J.J.A., Molinier, J., "Furfural Decarbonylation Catalyzed by Charcoal Supported Palladium: Part II- A Continuous Process", Biomass 16 (1988) pgs 89-96

[72] Gaset, K.J.J.A., Molinier, J., "Furfural Decarbonylation Catalyzed by Charcoal Supported Palladium: Part I-Kinetics.", Biomass 16 (1988) pgs 63-76

[73] Zeitsch, K.J., "The Chemistry and Technology of Furfural and its Many Byproducts", Elsevier Science, Amsterdam, pages 19, pages 19-27, 267-270, 2000

[74] Copelin, H. and Garnett, D.I., "Decarbonylation of Furfural", U.S. Patent 3,007,941, November 7, 1961

[75] Wambach, L., et al., "Preparation of Furan by Decarbonylation of Furfural", U.S. Patent 4,780,552, October 25,

presence of hydrogen in the gas phase has also been shown to suppress side reactions to oligomeric and polymeric compounds[77,78].

Evaluation of Liquid Phase Conversion of Furfural

Numerous laboratory experiments for liquid phase furfural decarbonylation in the pot of a batch distillation column were conducted to confirm the literature reports, and to support selection of the preferred process configuration.

A laboratory distillation column was fitted to the discharge port of a small scale batch reactor. Furfural and a KSE decarbonylation test catalyst were charged to the reactor, and nitrogen carrier gas fed through the vapor space of the reactor and through the column. The reactor was heated to refluxing temperature. Low boiling furan product was removed from the system in the nitrogen stream, which was sampled and analyzed by GC. After completion of the reaction, the remaining reactor contents were sampled and analyzed. Catalyst activity and furan selectivity were calculated from material balance and analytical results.

The liquid phase catalyst activity and selectivity compared to gas phase results with nitrogen reaction gas are summarized in Table 4. The gas phase results are discussed in detail below.

**Table 4**
**Gas Phase Decarbonylation Activity and Selectivity Superior to Liquid Phase**

| Reaction Phase | Reaction Temperature, °C | Furfural Conversion % | Reaction Rate Constant, $Min^{-1}$ | Furan Selectivity, % | Run Number |
|---|---|---|---|---|---|
| Liquid | 157 | 17 | 0.00057 | 41 | CHEMR19W |
| Liquid | 158 | 47 | 0.00134 | 70 | CHEMR25W |
| Gas | 100 | 18 | 4 | 94 | CHEMR52Y |
| Gas | 112 | 40 | 12 | 94 | CHEMR44W |

Catalytic activity for gas phase decarbonylation is 3 to 4 orders of magnitude higher than for liquid phase decarbonylation. Liquid phase reaction times were in the range of 4 to 5 hours, while gas phase catalyst contact times are in the range of 1 to 2 seconds.

Decarbonylation selectivity to furan is also far superior for gas phase reaction. Although no GC peaks other than furfural, furan, and carbon monoxide were observed in the analysis of either the carrier gas or liquid analyses, formation of oligomeric compounds represented about 30% of converted furfural for liquid phase service. Also, for the liquid phase reactions, significant amounts of water were formed in the final reaction mixture, typical of condensation reactions. The liquid phase reaction mixture also became increasingly dark colored as the reaction proceeded. These observations are all consistent with the production of large amounts of oligomeric and polymeric species by condensation reactions in the liquid phase reactions.

The results shown in Table 4 confirm that gas phase reaction is preferred, and therefore the preferred reactive distillation catalyst configuration is the side-car reaction. The side-car configuration will readily accommodate full gas phase reaction, along with broad flexibility in selection of reaction conditions in the side-car reactor.

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1988

[76] Li, K. and Ozer, R., “Vapor-Phase Decarbonylation Process”, U.S. Patent 8,404,871, March 26, 2013

[77] Wambach, L., et al., “Preparation of Furan by Decarbonylation of Furfural”, U.S. Patent 4,780,552, October 25, 1988

[78] Li, K. and Ozer, R., “Vapor-Phase Decarbonylation Process”, U.S. Patent 8,404,871, March 26, 2013

Based on these results, most catalyst screening studies were conducted under gas phase reaction conditions.

## Catalyst Activity Screening

The 15 Phase I catalysts, including a conventional Pd/Carbon catalyst, were evaluated for furfural conversion activity using laboratory scale tubular plug flow vapor reactor, to simulate the side-car reactor. Reactors were approximately 1 cm diameter and 10 cm length, and contained 5 to 10 grams of catalyst. Selection of reactor metallurgy was necessary to avoid wall-catalyzed reactions in the laboratory reactors having high surface to volume ratio. The reactors were provided with heating media, insulation, and temperature measurement and control devices to establish and maintain the reactor and its contents at a constant temperature within the range between 100°C and 300°C. Reaction pressure was atmospheric. Hydrogen from a pressurized cylinder was metered to merge with a furfural stream from a metering pump to be vaporized and fed to the catalyst bed. The stream exiting the tubular reactor was sampled and analyzed by FID gas chromatography (GC). Since CO is a byproduct of decarbonylation reactions, a second GC equipped with a methanizer was used for CO analysis. Four GC's are typically operated with sample carousels 24/7, being shut down to remove and reload samples. Data from the GC's are transmitted directly to laboratory computers for data workup and tabulation. Extensive QA/QC activities are maintained to assure faithful calibration and reliable sample analyses.

Catalyst activities for furfural conversion were described and compared according to a calculated pseudo-first order rate constant. For a first order reaction, the furfural conversion rate is defined as:

$$\text{Furfural conversion rate} = k\,[\text{Furfural}] \qquad (2)$$

Here, k is the pseudo-first order rate constant, and [Furfural] is the concentration of furfural in the feed gas stream. For a plug-flow reactor, Equation (2) takes the form:

$$-k\,\theta = \ln(1-x) \qquad (3)$$

where:

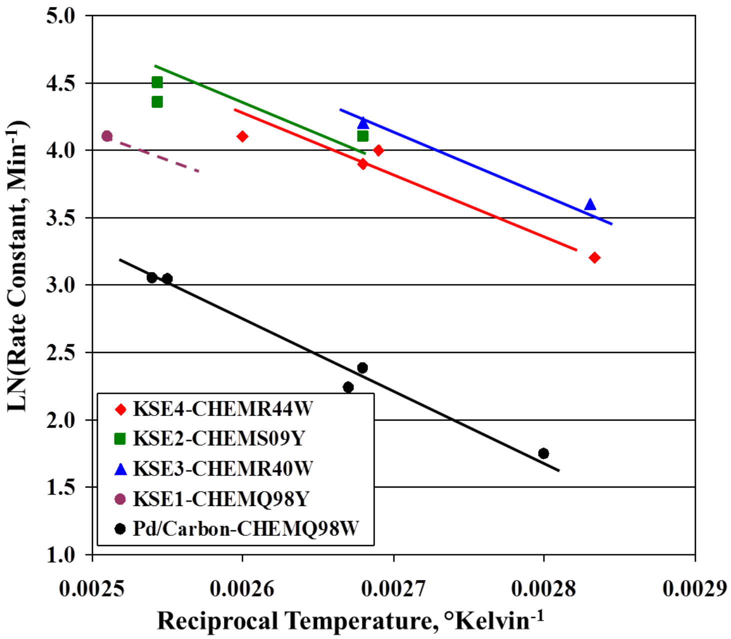
-k is the first order rate constant
-x is the fractional conversion of furfural
-θ is the reactor space time, defined as the catalyst volume divided by the volumetric flow rate to the reactor.

The pseudo-first order rate constant as defined above was used throughout the Phase I program for approximate description and comparison of relative catalyst activity.

The KSE catalysts were found to provide far higher activity than conventional catalysts traditionally used for furfural conversion.

Figure 5 shows an Arrhenius plot, using first order rate constants for the four best performing Phase I catalysts, compared to a conventional 1% palladium on activated charcoal catalyst.

**Figure 5**
**Arrhenius Comparison of Pseudo-First Order Rate Constants**
**KSE Phase I Catalysts Provide Dramatically Superior Furfural Conversion Activity**



As shown in Figure 5, the novel KSE catalysts for the decarbonylation and hydrogenation of furfural will provide catalytic activity for furfural conversion in the range of 2 to 3 orders of magnitude greater than conventional Pd/Carbon catalysts (note that the scale of the ordinate of Figure 5 is a logarithmic scale).

Catalyst Selectivity Evaluations

The highest activity catalysts for furfural conversion were extensively evaluated for reaction products and byproducts. Reaction and analytical procedures were the same as described above for catalyst activity evaluations. High precision gas chromatography procedures, combined with rigorous carbon balances, were used to insure that all reaction products and byproducts were properly identified and quantified.

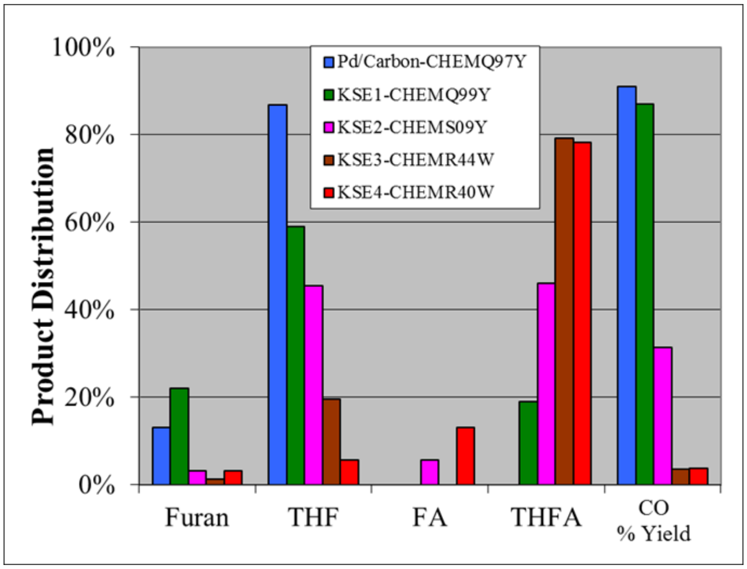
The primary reaction products identified were furan, tetrahydrofuran (THF), furfuryl alcohol (FA), and tetrahydrofurfuryl alcohol (THFA). The reaction pathways described above in Figure 3 also indicate the possible production of 1,5 pentanediol and various $C_4$ and $C_5$ alcohols and aldehydes by furan ring opening reactions. As discussed below, one KSE catalyst was found to produce 1,5-pentanediol. No $C_4$ and $C_5$ alcohols and aldehydes were detected in any of the Phase I experiments.

Small quantities of an unidentified compound were produced in a few of the experimental runs. This unknown was accounted for in material and carbon balances by assuming a GC response factor equivalent to furfural. Other observed byproducts included carbon monoxide (CO). CO is the expected byproduct of decarbonylation reactions. The identity of the unknown compound will be clarified as part of the Phase II program.

Because of the multiple parallel reactions pathways, each with sequential reactions, catalyst selectivity performance must be compared at comparable catalyst activity and overall furfural conversion. Results from the catalyst activity studies were used to select reaction conditions for each catalyst to allow catalyst selectivity comparison at comparable catalyst activity and furfural conversion level.

The product distributions for the highest activity KSE Phase I catalysts, along with the conventional Pd/carbon catalyst, are shown in Figure 6 below. The % yield of CO, calculated as moles of CO produced per mole of furfural converted, is also included as a marker for the decarbonylation reaction pathway.

**Figure 6**
**KSE Phase I Catalysts Demonstrate Exceptionally High Activity**
**For Hydrogenation Reactions**



The high CO yield confirms that the product distribution is achieved by decarbonylation of furfural to furan, with subsequent hydrogenation to THF. The product distribution obtained with Phase I catalysts at these conditions of Figure 6 make both furan and THFA. These compounds can be readily converted to THF with additional hydrogenation, and a trim hydrogenation unit has been added to the process design of Task 3 to assure that 100% THF can be achieved.

For Figure 6, the reaction temperature and catalyst contact time were selected to provide comparable catalyst activity and furfural conversion. Under the specific reaction conditions used for the Figure 6 comparison, Phase I catalysts KSE3 and KSE4 gave a product distribution containing nearly 80% tetrahydrofurfuryl alcohol (THFA). The low CO yields are consistent with furfural conversion primarily by sequential hydrogenation of furfural to furfuryl alcohol (FA) and THFA. However, in order to achieve comparable catalyst activity and furfural conversion, the product distribution for catalysts KSE2 and KSE4 was evaluated at a temperature 100°C lower than for the conventional Pd/Carbon catalyst.

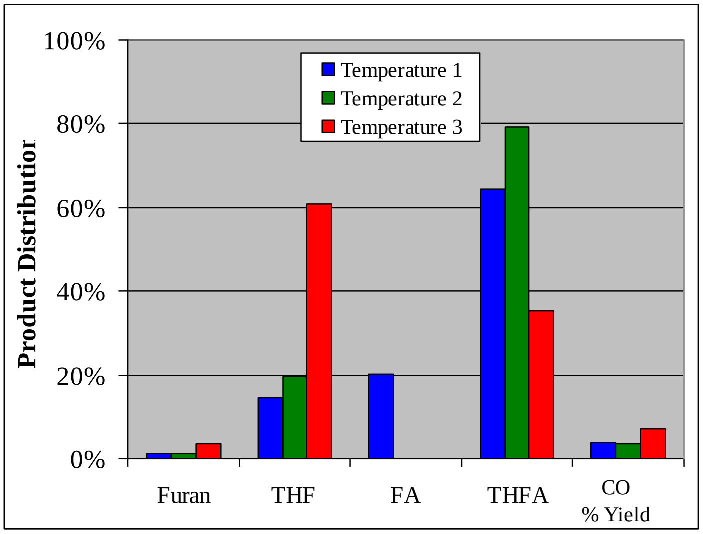
The extremely high catalytic activity of the KSE catalysts KSE3 and KSE4 for hydrogenation reactions, indicated by Figure 5 and the product distribution shown in Figure 6, is very surprising. Although furfural decarbonylation is often conducted at pressures at or near atmospheric pressure, and temperature in the range of 160°C, hydrogenation reactions are typically conducted at much higher temperatures and pressures.

These results have profound consequences for the advantages of a reactive distillation process. The extremely high hydrogenation activity indicates that the furfural decarbonylation and hydrogenation reactions can indeed be conducted with the same catalyst and in the same reaction environment, at temperatures and pressures that are consistent with a reactive distillation column.

Both THF (66°C boiling point) and furan (31°C boiling point) have azeotropes, and are very volatile, and far more volatile than furfural, water, and other components. When the discharge stream from the vapor phase side car reactor is returned to the column, both the THF product, and any remaining furan, will be rapidly driven to the top of the column for take off as a vapor stream. Unconverted furfural will be picked up by the vapor and liquid streams in the reactive distillation column, for recycle by the column VLE/LLE back to the side draw location for the reactor. Water and heavier components will be driven to the bottom of the column for discharge. All of these separations, and recycle of unconverted furfural, occur within the single reactive distillation column without the need for the additional separation steps and recycle streams used in conventional processes. This results in substantial process intensification, a recognized hallmark of reactive distillation technology.

The product distribution can be altered by changing the reaction conditions. Figure 7 shows the product distribution and CO % yield for catalyst KSE3 at three different reactions temperatures. Since catalyst contact time remained constant during these experiments, furfural conversion also increases as temperature is increased. Increasing reaction temperature and furfural conversion greatly increases the reaction selectivity to THF. Since the CO yield remains nearly constant for all three reaction conditions, it is likely that the increased THF production is achieved primarily by hydrogenolysis of THFA rather than by the furfural decarbonylation pathway. This is consistent with results reported by Zheng, et al[79].

**Figure 7**
**Product Distribution Can Be Controlled by Selection of Reaction Conditions: Run CHEMR40W**



During these catalyst activity and selectivity evaluations, one of the KSE Phase I catalysts was found to produce measurable levels of 1,5-pentanediol by furan ring opening reactions. As discussed above, 1,5-pentandiol represents a useful commercial product. The composition and structure of this catalyst should be further examined for possible optimization to a catalyst specifically selective to 1,5-pentanediol.

The concentration of furfural in the feed gas was also found to represent another key reaction parameter for catalyst selectivity. The Aspen process simulations indicated that a furfural concentration of about 10% in the hydrogen stream would be consistent with commercial operation for both the side car reactors, and total column vapor rates in the reactive distillation column after return of the side car reactor exit stream (including the hydrogen and CO gas components) back to the reactive distillation column. Simulations indicated that the presence of the gas components reduces the vapor phase partial pressures for furfural, water, and other components, effectively enhancing the in-column separations.

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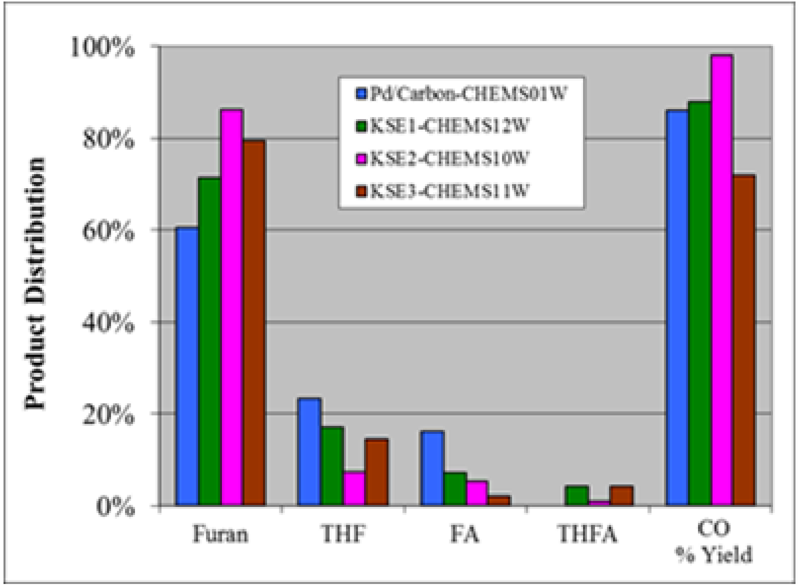
[79] Zheng, H-Y, et al., “Toward Understanding the Reaction Pathway in Vapor Phase Hydrogenation of Furfural to 2-Methylfuran”, Journal of Molecular Catalysis, Vol. 246, pages 18-23, 2006

To provide reaction data under conditions consistent with commercial operation, several of the highest activity catalysts were evaluated with furfural feed concentrations in the range of 10%.

In laboratory operations, the hydrogen feed was preheated. Parallel metering pumps were used, one pumping furfural and one pumping water. In this way, water concentrations exceeding that of the saturation level of furfural could be achieved. The two liquid streams were metered into the preheated hydrogen stream using high precision syringe pumps, and the resulting gas stream fed to the plug flow gas phase reactor.

The resulting product distributions for the conventional Pd/Carbon catalysts and three of the highest activity KSE Phase I catalysts are shown in Figure 8. Reaction conditions for the various catalysts were again selected to provide comparable activity and furfural conversion.

**Figure 8**
**KSE Phase I Catalysts Demonstrate High Selectivity to Furan and THF**



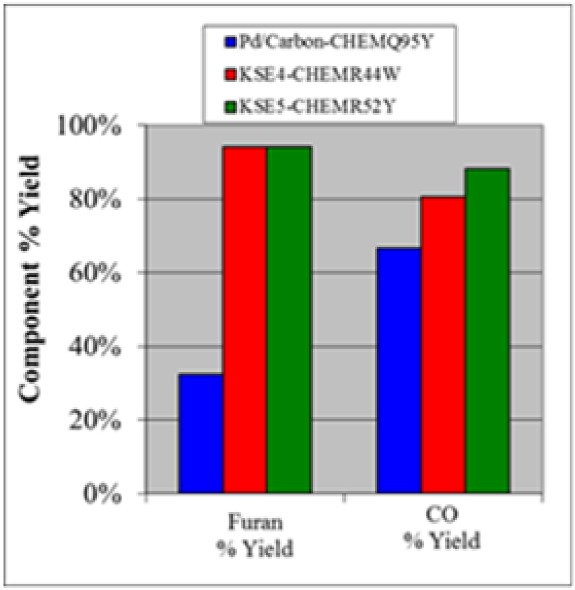
The increase in furfural feed concentration, and the corresponding decrease in the ratio of the hydrogen to furfural reactants, dramatically altered the balance between the furfural decarbonylation and hydrogenation pathways. Although there are significant differences among the catalysts in activity, under these reaction conditions, the Figure 8 catalysts provide a similar product distribution, with furan and THF as the primary products. CO yields were comparatively high for all catalysts, indicating that furfural decarbonylation is the primary reaction pathway.

For comparison of catalyst activity and selectivity, the data shown in Figure 8 was obtained at intermediate levels of furfural conversion. As a result, the hydrogenation of furan to THF was not completed. Hydrogenation of furan to THF, and hydrogenolysis of THFA to THF, can be readily completed by carrying the reaction to full conversion. For the Phase I KSE catalysts, this would provide an overall yield of THF from furfural approaching 100%. This can be achieved either by operating at very high conversion within the reactive distillation system itself, or by utilizing a separate simple tubular gas phase hydrogenation reactor down stream of the reactive distillation system. These process options will be further valuated as part of the Phase II program.

To gain further insight into the separate furfural decarbonylation and hydrogenation pathways, the conventional Pd/Carbon catalyst, and two Phase I KSE catalysts were evaluated using nitrogen as the feed gas instead of hydrogen. With nitrogen as the feed gas, hydrogenation reactions will be eliminated, leaving decarbonylation to furan as the only active reaction pathway. In addition, it is known that the presence of hydrogen in the reaction gas suppresses furfural loss due to side reactions[80,81]. Catalyst evaluations with nitrogen as the feed gas will therefore provide a stringent examination of the inherent selectivity of the catalysts for the decarbonylation reaction. Furfural side reactions are believed to result in oligomeric or polymeric substances which can deposit on catalyst active sites, also resulting in catalyst deactivation.

Yield results for furan and CO with nitrogen feed gas are shown in Figure 9 below.

**Figure 9**
**KSE Phase I Catalysts Demonstrate Superior Inherent Furfural Decarbonylation Selectivity**



As expected, furan yield for the conventional Pd/Carbon catalyst was very poor, indicating substantial loss to side reactions. No gas phase byproducts were identified, consistent with the formation of oligomeric or polymeric substances. The Pd/Carbon reactor plugged after extended operations. The KSE Phase I catalysts provided furan yield greater than 90%, along with significantly higher CO yield then the conventional catalyst. This clearly demonstrates the inherent superior decarbonylation selectivity of the KSE Phase I catalysts, and also indicates that the KSE catalysts may be far less prone to the generation of oligomeric and polymeric species. Since the deposition of polymeric byproducts on catalyst active sites has been proposed as a mechanism for the observed progressive deactivation of conventional furfural decarbonylation catalysts, the clear superiority of the KSE catalyst shown in Figure 9 may have profound implications for the stability of the KSE catalysts, as discussed below.

The data for Figure 9 was again taken with reaction conditions for each catalyst selected to provide similar catalyst activity and furfural conversion. Achieving similar activity and furfural conversion required evaluation of the conventional Pd/Carbon catalyst at a reaction temperature 80°C to 90°C higher than the KSE catalysts, indicating that the KSE Phase I catalysts are dramatically superior to conventional catalysts in decarbonylation activity as well as hydrogenation activity.

Effect of Water

The proposed commercial technology developed in this SBIR program will take a slip stream of

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[80] Wambach, L., et al., "Preparation of Furan by Decarbonylation of Furfural", U.S. Patent 4,780,552, October 25, 1988

[81] Li, K. and Ozer, R., "Vapor-Phase Decarbonylation Process", U.S. Patent 8,404,871, March 26, 2013

hydrolysate from a hardwood dissolved pulp mill, convert the xylan on the hydrolysate stream to furfural, and concentrate the furfural by use of a reactive distillation column.

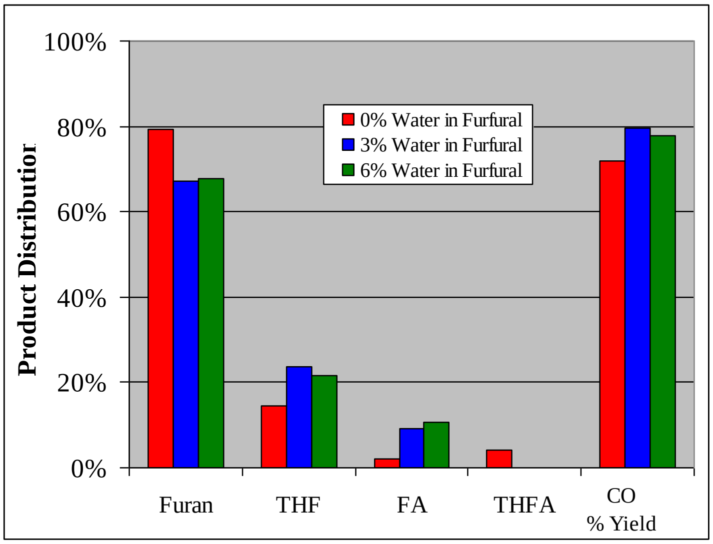
Extensive Aspen simulations on the reactive distillation process were used to define the water and furfural compositions throughout the column. Azeotropic distillation allows the furfural to be rapidly concentrated in the column. When the total boiling liquid mixture is concentrated to contain 20% furfural or more by mass, the liquid will phase separate, forming two liquid phases. The resulting furfural rich phase, containing approximately 6% water, is extracted and vaporized to form the feed stream for the vapor phase side car reactor. The vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) characteristics of furfural and water can be used to effectively "fine tune" the furfural/water composition in the feed to the side car reactor (see Task 3 for reactive distillation process description and discussion of the reactive distillation simulations).

Aspen process simulations indicate that the water content of the column side draw stream for feed to the gas phase side car reactor will be about 6%. Since the presence of water can be detrimental to furfural conversion selectivity by driving hydrolysis side reactions[82], the effect of water in the feed gas to the reactor was evaluated. Furfural with water added at levels of 3% and 6% was used as feed stock. These differing water levels can be thought of as trays in the reactive distillation column, where water levels are controlled through the column. A choice of water content of the furfural can be made be choosing the specific location for the side stream draw for feed to the side car reactor. The concentration of furfural in the overall feed stream was 10%.

Compared to reaction results with no water present, furfural conversion and catalyst activity were found to be unchanged with 3% and 6% water in the furfural feed. As shown in Figure 10, there is no significant change in the overall product distribution with either 3% or 6% water in the furfural feed stock. This confirms that the concentration of furfural in the reactive distillation column to a feed composition containing about 6% water is valid.

**Figure 10**

**Water at 6% in Furfural Feed Stock Does Not Affect Catalyst Selectivity**



Catalyst Stability Evaluations

Conventional furfural decarbonylation catalysts are known to suffer from catalyst deactivation,

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[82] Copelin, H. and Garnett, D.I., "Decarbonylation of Furfural", U.S. Patent 3,007,941, November 7, 1961

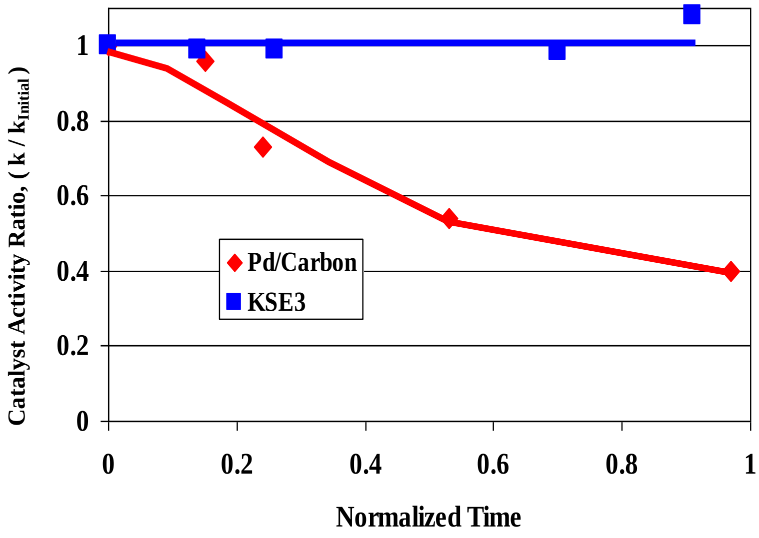
requiring periodic regeneration with air and steam at elevated temperature[83,84]. One of the KSE Phase I catalysts, along with the conventional Pd/Carbon catalyst, were evaluated for an extended run time to assess catalyst stability. Hydrogen was used as the reaction feed gas for these evaluations, along with furfural concentrations in the range of 10% to represent actual expected commercial operation.

Figure 11 shows the relative catalyst activity, the ratio of the catalyst activity at any run time divided by the initial activity at he start of the run, as a function or run time. Run time is shown in Figure 9 as a normalized time, where actual time is divided by the longest time for either of the two runs.

Figure 11 demonstrates that, as expected, the activity of the conventional Pd/Carbon catalyst decreases steadily, losing about 60% of its initial activity over the duration of the evaluation. The KSE Phase I catalyst fully retains 100% of its initial value for the duration of the test. Since the deactivation of conventional catalysts is believed to be due to the deposition of oligomeric or polymeric furfural reaction byproducts on catalyst active sites, the superior performance if the KSE Phase I catalysts is likely due to their far superior decarbonylation selectivity, as shown in Figure 9 above.

CO, an inevitable byproduct of decarbonylation reactions, is known to be a poison for noble metal catalysts, also resulting in catalyst deactivation. It is possible that the presence of high levels of hydrogen in the feed gas may effectively provide continuous catalyst reduction, thereby suppressing CO deactivation. Addition of other metal promoters, such as cesium, which can mitigate poisoning, will be studied further in the Phase II program. As previously stated, no deactivation has been seen with the KSE Phase I catalysts.

**Figure 11**
**KSE Phase I Catalysts Demonstrate Superior Stability**



Longer stability tests will be conducted during the Phase II program, along with experiments to identify the specific mechanism for any observed deactivation.

In summary, the Task 2 catalyst and reaction process evaluations have demonstrated that:

- Side car reactive distillation is the preferred process configuration for the conversion of a dilute aqueous furfural stream to THF:

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[83] Wambach, L., et al., “Preparation of Furan by Decarbonylation of Furfural”, U.S. Patent 4,780,552, October 25, 1988

[84] Li, K. and Ozer, R., “Vapor-Phase Decarbinylation Process”, U.S. Patent 8,404,871, March 26, 2013

  - The exceptional activity and selectivity performance of the KSE Phase I catalysts allows for furfural decarbonylation and hydrogenation reactions to be conducted simultaneously in a gas phase side car reactor at pressures and temperatures consistent with conditions in the column.
  - The column, in combination with the side draw and return streams for the side car reactor, effectively utilizes the vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) characteristics of furfural, water, and other components to rapidly concentrate the furfural from the dilute aqueous solution to a composition consistent with high selectivity conversion to furan and THF by the KSE catalysts in the side car reactor. This is discussed in more detail under Task 3.
  - The column utilizes the return stream from the side car reactor, without the requirement for any additional separation steps, to:
    - Rapidly drive the THF and furan reaction products to the top of the column for gas phase take off.
    - Recycle unconverted furfural in the side car reactor exit stream back to the reactor side draw location.
    - Drive water and other heavy components to the bottom of the column for discharge.

- The new KSE catalysts for the selective decarbonylation and hydrogenation of furfural provide exceptional catalytic activity, exceeding the activity of conventional furfural conversion catalysts by 2 to 3 orders of magnitude.
- The new KSE catalysts, under the most stringent conditions, are highly selective for furfural decarbonylation, and far superior to conventional catalysts for furfural conversion. The feasibility of producing THF with overall selectivity approaching 100% has been demonstrated.
- The new KSE catalysts have demonstrated stability characteristics dramatically superior to conventional furfural decarbonylation catalysts.
- Water levels consistent with process simulations of the reactive distillation process do not affect catalyst activity or selectivity.
- The new catalysts and overall reaction process can potentially produce other commercially valuable products, such as tetrahydrofurfuryl alcohol, 2-methyltetrahydrofuran, or 1,5-pentandiol as co-products with THF. The product distribution can be readily controlled by varying process operating conditions such as reaction temperature, furfural conversion level, and furfural feed concentration.

## TASK 3. PROCESS DESIGN, SIMULATION, AND ECONOMIC STUDIES

For successful completion of the Phase I feasibility study, a process design and cost estimate was performed for the novel KSE iCARD technology for production of THF from a dilute aqueous hydrolysate from operation of a dissolved pulp mill. These design estimates have faithfully reflected the demonstrated performance of the Phase I experimental program. The process design and cost estimation were developed using the Aspen ONE process simulation software, a powerful simulation tool widely used in the industry, to test various aspects of the process and build a working simulation model of the process from hydrolysate to purified THF. The cost analysis was developed using the Aspen ONE Process Economic Analyzer, supplemented by engineering cost analysis and vendor quotes as necessary.

The Aspen ONE process simulations were also used to assist the laboratory program, and laboratory results were used to update the thermodynamic properties of the biomass products. A critical aspect of these models is the thermodynamic properties and parameters describing all components of the system and their interactions. The Phase I process design was based on properties for pure components and mixtures that are obtained from three sources: (1) literature values obtained from databases such as Dechema, Detherm, and NIST, (2) models based on KSE laboratory results, and (3) estimates via various methods included in Aspen One. During the Phase II program, models for the nonideal phase behavior of reaction mixtures of xylose, furfural, water, furan, THF, and other system components will be further developed and validated.

### Historical Manufacturing Technology for THF

Essentially all current U.S. production of THF is based in the dehydration of 1,4-butanediol (BDO) with an acid catalyst. The production of THF is by far the largest single use of BDO, representing 50% of BDO use[85]. BDO is produced by a variety of reaction paths[86,87]:

- The reaction of acetylene and formaldehyde to form 2-butyne-1,4-diol, followed by hydrogenation to BDO.
- Oxidation of propylene to propylene oxide, followed by isomerization to allyl alcohol. Allyl alcohol is then converted by hydroformylation to 4-hydroxybutyraldehyde, followed by hydrogenation to BDO
- Acetoxylation of butadiene to 1,4-diacetoxy-2-butene, followed by hydrogenation to 1,4-diacetoxybutane, and hydrolysis to produce BDO.
- Oxidation of butane to maleic anhydride, followed by etherification to diethyl maleate and hydrogenation to BDO, the common process installed since 1990.

All of the above production chains, starting from the basic hydrocarbon feed stocks, such as propylene, butane, acetylene, or butadiene, to BDO, are extremely lengthy, complex, energy intensive, and costly. Although all of the above pathways are known to be used commercially, the butane-maleic anhydride pathway appears to be the most common[88]. Recently, technology for the direct co-production of BDO and THF from maleic anhydride was introduced[89].

THF has been produced on a limited basis from biomass feedstocks in the past, using furfural and furan as key intermediates. However, the conventional technology for converting furfural to THF requires a feed stream of purified furfural. Conversion of a dilute biomass hydrolysate to purified furfural is extremely difficult and energy-intensive, due to the low concentration aqueous solution, the presence of furfural-water azeotropes (~10%), and side reactions occurring at distillation temperatures. This technology is not currently practiced for commercial production of THF.

The BDO and maleic anhydride co-production routes to THF, and the raw material costs associated with those routes, have been used for competitive comparisons to the new KSE technology for production of THF from dilute aqueous furfural solution.

## KSE Reactive Distillation Process for Production of THF from Pulp Mill Hydrolysate

### Feedstock for the KSE Process

The Phase I KSE Selective decarbonylation-hydrogenation technology is based on the use of a dilute aqueous furfural, along with hydrogen, as the primary reactants for the catalytic decarbonylation and hydrogenation to produce THF. Many pulp and paper mills currently utilize a process termed "Kraft pre-hydrolysis", which extracts wood chips with hot water prior to intensive digestion[90]. The resulting

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[85] "Chemical Profile, 1,4-Butanediol", ICIS Chemical Business, http://www.icis.com/Articles/2009/03/02/9195785/chemical+profile+14-butanediol.html

[86] "Tetrahydrofuran", Ullmann's Encyclopedia of Industrial Chemistry, Wiley VCH, Wienheim, 2012

[87] Whitcoff, H.A., et al., "Industrial Organic Chemicals", John Wiley & Sons, New York, pages 349-351, 2004

[88] "Tetrahydrofuran", Ullmann's Encyclopedia of Industrial Chemistry, Wiley VCH, Wienheim, 2012

[89] "Butanediol and Co-Products, Davy Process Technology; http://www.davyprotech.com/pdfs/Butanediol%20and%20Derivatives.pdf

[90] "Continuous Pre-hydolysis Kraft Cooking", Continuous Pulping Processes, TAPPI; http://www.sugarresearch.library.qut.edu.au/114/1/Continuous_Pulping_Processes.pdf

hydrolysate stream from hard wood chips consists of a dilute solution of 5-carbon pentosan hemicellulose and pentose sugars[91]. Such 5-carbon sugars are readily converted to furfural by established commercial scale technology[92], and represent an ideal base raw material for production of THF. Currently, this stream is concentrated by water removal, and burned[93]

Hot water hydrolysis is an effective extraction technique for the hemicellulose fraction of woody biomass. The hemicellulose fraction is particularly soluble in water and the lack of aggressive chemicals reduces the decomposition of the pentosan material contained in the hemicellulose. This stream can then be sent directly to the KSE reactive distillation process for the reaction of the pentosan fraction of the dissolved biomass into furfural. Non-pentosan components of the hydrolysate stream, and any by-products of the non-pentosan components, represent very high boiling compounds, and will be removed from the process as described below. This material can then be returned to the pulp mill for use as fuel to power the mill.

A known byproduct of the hot water pre-hydrolysis of woody biomass is acetic acid. Because of the comparatively low boiling point, and potential reactivity of acetic acid, it was included as part of the process simulations in order to track its migration in the reactive distillation column and provide a design basis for the number of stages needed to drive the acetic acid, and other anticipated biomass components, down the column.

A typical pre-hydrolysis hydrolysate will contain about 2.3% pentosan/pentose, 1.2% acetic acid, 1.6% soluble lignin and other heavy components, and the balance water[94]. This stream composition was used as the feedstock for the KSE reactive distillation process.

The chemistry and technology for the conversion of pentosan solutions to furfural using mineral acid catalysts is well established and extensively documented[95,96,97]. As part of the Phase I process design, it was assumed that conventional mineral acid catalysts, along with reaction compositions, and reaction conditions detailed in the scientific literature, would be utilized to convert the pentosan/pentose fraction of the hydrolysate stream to furfural for conversion to THF by the KSE selective catalytic decarbonylation and hydrogenation of furfural.

KSE Reactive Distillation Technology

A schematic diagram of the KSE reactive distillation process for the selective decarbonylation and hydrogenation of dilute aqueous furfural is shown in Figure 12 below.

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[91] Heiningen, A., “Integrated Forest Product Refinery”, Final Report, DOE FC36-04GO14306, May 29, 2010

[92] Zeitsch, K.J., “The Chemistry and Technology of Furfural and Its Many By-Products”, Elsevier Scienec B.V., Amsterdam, pages 1-74, 2000

[93] “Continuous Pre-hydrolysis Kraft Cooking”, Continuous Pulping Processes, TAPPI; http://www.sugarresearch.library.qut.edu.au/114/1/Continuous_Pulping_Processes.pdf

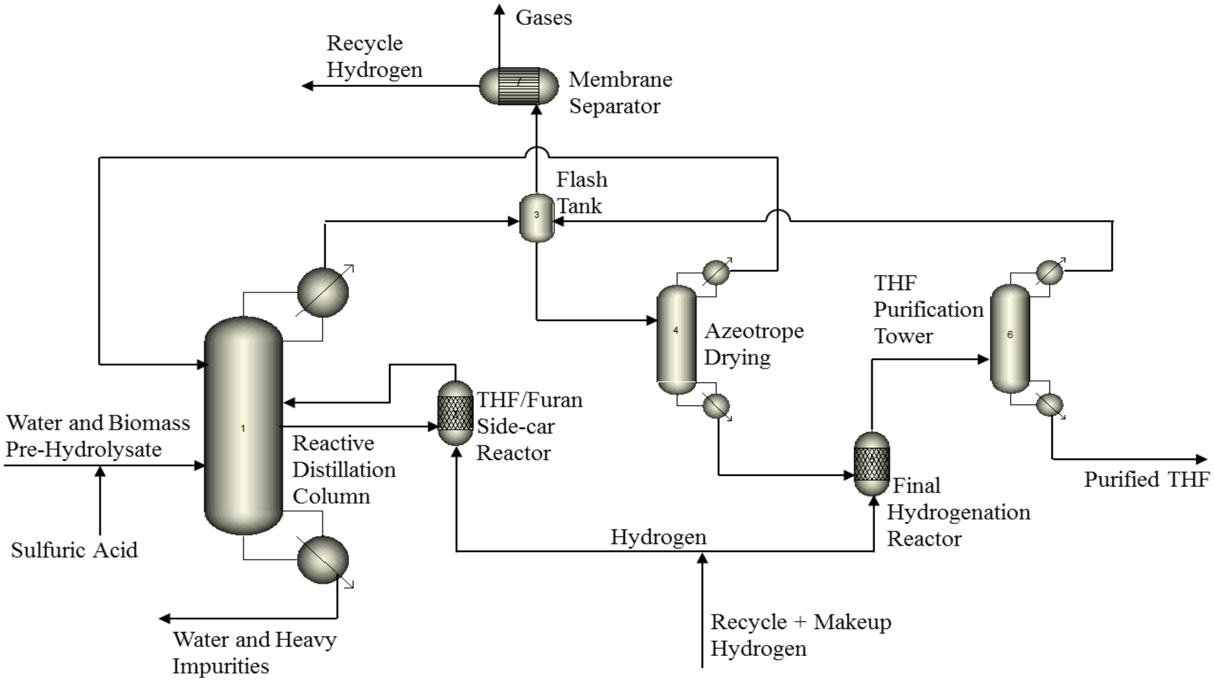
[94] Van Heiningen, A., Forest Bioproducts Research Institute, University of Maine, private communication, 10/3/2013

[95] Zeitsch, K.J., “The Chemistry and Technology of Furfural and Its Many By-Products”, Elsevier Scienec B.V., Amsterdam, pages 1-74, 2000

[96] De Jong, W. and Marcotullio, G., “Overview of Biorefineries Based on Co-Production of Furfural, Existing Concepts and Novel Developments, International Journal of Chemical Reactor Engineering, Vol. 8, Article A69, 2010

[97] Binder, J.B., et al., “Synthesis of Furfural from Xylose and Xylan”, ChemSusChem, Vol. 3, pages 1268-1272, 2010

**Figure 12**
**KSE Reactive Distillation Process for the Selective Decarbonylation and Hydrogenation of Hydrolysate to THF**



The hydrolysate stream, described above, is fed to the reactive distillation column. The mineral acid conversion of the pentosan/pentose component to furfural is conducted in the distillation pot of the reactive distillation column. The soluble lignin and other heavy components remain in the distillation bottoms, and are discharged as part of the bottoms stream.

The main process distillation column has three exit streams and takes advantage of the physical and thermodynamic properties of many of the anticipated chemical constituents. Water, acetic acid and furfural each boil as pure components at 100 °C, 118 °C, and 161.4 °C respectively. The difficulty of separating acetic acid and water, due to the extremely pinched VLE behavior is well known, especially for dilute concentrations of acetic acid in water[98],[99]. This phenomenon actually works in favor of the separation process between acetic acid and furfural. Furfural and water form an azeotrope which boils at 97.8 °C. This azeotrope acts as the unstable node in the distillation, and furfural is actually driven upwards through the column despite its high pure component boiling point. The acetic acid remains in the bottom of the column, and is removed as part of the bottoms stream.

The azeotropic composition of furfural and water at atmospheric pressure is 35.5% and 64.5% respectively by mass. The volatility of this azeotrope, when compare to that of pure water, is also noteworthy. For mixtures of furfural and water, low concentrations of furfural in the liquid phase increase many times over in the vapor phase as the mixture boils, allowing rapid concentration of the furfural within the column.

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[98] Othmer, D.F. Separation of Water from Acetic Acid by Azeotropic Distillation. Ind. Eng. Chem. (1935) 27 (3) pp 250-255

[99] Berg, L. “Dehydration of acetic acid by azeotropic distillation.” US Patent 5,160,412 March 10, 1992

Another important property of furfural-water mixtures that is exploited in the main column is the formation of a second liquid phase. When the total boiling liquid mixture is concentrated to contain 20% furfural or more by mass, the liquid will phase separate, forming two liquid phases. The resulting furfural rich phase, containing approximately 6% water, is extracted and vaporized to form the feed stream for the vapor phase side car reactor. As described under Task 2 above, both catalytic activity and selectivity for the decarbonylation and hydrogenation of furfural greatly favor vapor phase reaction.

The vaporized furfural stream, along with hydrogen, serves as the basis of the feed to the side car reactor, containing the KSE selective decarbonylation and hydrogenation catalysts. As described under Task 2 above, reaction products include furan, furfuryl alcohol, tetrahydrofuran, and tetrahydrofurfuryl alcohol. The product distribution can be controlled by catalyst selection and reaction conditions to provide either a highly selective THF product, of THF with co-products such as tetrahydrofurfuryl alcohol.

The exit stream from the side car reactor is returned to the primary column for separation of the highly volatile furan and THF reaction products from unconverted furfural, and any higher boiling reaction products, such as furfuryl alcohol or tetrahydrofurfuryl alcohol. The lighter components, furan and THF, along with the gases carbon monoxide and hydrogen, are driven out the top of the column as a vapor phase take off, and are sent downstream for further processing into the final THF product. Unconverted furfural and other heavy components are allowed to fall back down the column and equilibrate with the furfural distillation from the feed. The heavy impurities are eventually removed from the bottom of the distillation column along with water.

The hydrogen and carbon monoxide gases from the column overhead are separated, and the furan and THF reaction products are dried in a drying column. The low boiling point of the THF/furan mixture in the bottoms of the drying column, approximately 40°C, allows the drying column to operate on a waste heat source. These process components are relatively small, and are not shown in the Figure 11 schematic diagram.

The dried THF/furan stream, consisting of THF and furan, is sent to the vapor phase THF reactor, where the hydrogenation of furan to THF is completed. Based on the results of the Phase I program, as discussed under Task 2, although a substantial amount of hydrogenation, and THF production, does occur within the reactive distillation system, it may not be desirable to complete the full hydrogenation of furan to THF within the primary reactive distillation system. The process option for completing the hydrogenation reactions within the primary reactive distillation column, or utilizing a hydrogenation finishing reactor, as shown in Figure 12, will be further evaluated during the Phase II program.

The exit stream from the THF finishing reactor is purified by removal of dissolved gases and light ends in a THF purification column to meet commercial THF specifications.

Process Design and Economics

The KSE iCARD catalytic reactive distillation technology for THF manufacture will utilize hydrolysate generated during the commercial operation of a dissolving pulp mill. The design basis manufacturing capacity of a full scale commercial facility for manufacture of THF from pulp mill hydrolysate was selected to be consistent with the hydrolysate production capacity of a single typical North American dissolving pulp mill. Table 5 below summarizes the capacity of ten selected North American pulp mills producing dissolving pulp, not the total North American capacity.

**Table 5**
**Typical North American Dissolving Pulp Mills**[100]

| Pulp Mills Producing Dissolved Pulp | Dissolving Pulp Capacity, MTPA |
|---|---|
| Buckeye Technologies, Memphis, TN | 465,000 |
| Buckeye Technologies, Perry, FL | 515,000 |
| Rayonier , Jesup, GA | 330,000 |
| Rayonier, Fredonia, FL | 155,000 |
| SAPPI, Cloquet, MN | 525,000 |
| SAPPI, Somerset, ME | 330,000 |
| Cosmo Specialty Fiber, Cosmopolis, WA | 140,000 |
| Mercer International, Celgar, Canada | 400,000 |
| Mercer, International, Stendal, Canada | 500,000 |
| Fortress Paper Ltd., Thurso, Canada | 200,000 |

Dissolving pulp manufacture will typically produce hydrolysate containing 90 tons of xylan/xylose for every 1000 metric tons of dissolving pulp produced[101]. If all of the xylan/xylose is converted to THF, this would result in the production of about 44 metric tons of THF for each 1000 metric tons of dissolving pulp produced.

Based on the above table, a typical dissolving pulp mill, such as the Rayonier plant in Jesup, GA, produces 330,000 metric tons per annum (MTPA) of pulp. Hydrolysate from such a plant would therefore be capable of producing about 15,000 MTPA of THF, or about 32 million pounds per year. Based on a typical dissolving pulp mill with 330,000 MTPA pulp capacity, the design basis for a commercial THF plant in our Phase I project for development of the iCARD catalytic reactive distillation technology was selected as 32 million pounds per year of THF.

A 32 million pound per year capacity would represent about 10% of the estimated U.S. THF market of about 320 million pounds per year. Just the ten plants listed above, if fully equipped with THF production capacity based on the KSE iCARD catalytic reactive distillation technology, would accommodate over 100% of the estimated U.S. THF market.

For the design and economic study, a THF production rate of 32 million pounds per year was used as the design basis. This is consistent with the production rate of hydrolysate byproduct stream for a pulp mill with a 300,000 ton per year capacity. There are numerous domestic U.S. pulp mills, utilizing hot water pre-hydrolysis, with a pulp production capacity in this range.[102]

Such hydrolysate byproduct streams are currently concentrated and burned as fuel to supply steam and power to the pulp mill. The value of the pentosan component of the hydrolysate stream was determined by calculating the combustible energy contained within the pentosan and the purchase requirement of natural gas necessary to replace the lost energy. This determination is shown below in Table 6 and 7, based on the production of 32 million pounds of THF annually.

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[100] "Pulp Mills and Pulp Manufacturers", http://www.paperonweb.com/manf.htm

[101] "Plaice, M., "Bioproducts from Dissolving Pulp Manufacturing", FPInnovations, January 13, 2009
**Http://*www.lifesciencesbc.ca/files/Event_Presentations/Othe_Events./5-Paice_(2).ppt***

[102] FPInnovations and Paprican presentation on bioproducts from dissolving pulp manufacturing, https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&ved=0CCkQFjAA&url=http%3A%2F%2Fwww.lifesciencesbc.ca%2Ffiles%2FEvent_Presentations%2FOther_Events%2F5Paice_(2).ppt&ei=CRSmUqLTEcrWkQfQiIGIDA&usg=AFQjCNHoJB0vYs1EGYtD4M55O0nAzQ0k6Q&bvm=bv.57752919,d.eW0 (Accessed November 18, 2013)

**Table 6**
**Biomass Raw Material Cost for KSE Reactive Distillation Process to THF**

| Determination Of The Fuel Value Of Pentosan For The KSE Process | | |
|---|---:|---|
| Annual Feed Production Of THF | 32,369,473 | lbs/yr |
| Furfural Feed Requirement | 45,179,331 | lbs/yr |
| Xylose Feed Requirement | 70,590,877 | lbs/yr |
| Xylose Heating Value | 0.0067 | MMBtu/lbs |
| Energy Provided From Combustion Of Xylose | 473,672 | MMBtu/yr |
| Cost Of Natural Gas (U.S. National Average) | $4.52 | USD/MMBtu |
| Annual Cost To Replace Xylose With Natural Gas | $ 2,141,292 | USD/MMBtu |

**Table 7**
**Additional Raw Material Costs for KSE Reactive Distillation Process to THF**

| Other Feed Costs Included In The KSE Process | | |
|---|---:|---|
| 1.5% Sulfuric Acid Requirement On Hydrolysate Stream | 23,019 | tons/yr |
| Cost Of Sulfuric Acid In Bulk | $ 71.00 | USD/ton |
| Annual Cost Of Sulfuric Acid | $ 1,638,936 | USD/yr |
| Hydrogen Consumed In Process Reactors | 1,846,835 | lbs/yr |
| Cost Of Hydrogen On A Mass Basis | $0.91 | USD/lbs |
| Annual Cost Of Hydrogen Gas Consumed | $ 1,675,420 | USD/yr |

Both the traditional process routes to THF require hydrogen and catalysts at some point in the process but these costs were not explicitly included in the raw materials cost of these processes. This is due to the general observation that the traditional routes to THF are built within larger plants that produce other chemicals. It is anticipated that the source of hydrogen present for both of these traditional processes is obtained at a lower cost than it can be for our process. Due to the nature of the product manufactured at pulp and paper mills it is not expected that hydrogen would be readily available natively from the mill. The cost of hydrogen used in the economic analysis for the KSE route is based off hydrogen production from natural gas.[103] Catalyst costs were not included in the raw material cost for the traditional routes due to their general construction from different lower cost materials.[104,105,106,107]

Further economic analysis for the KSE process was performed using the process simulation completed in Aspen Plus producing 32 million pounds annually and the Aspen Process Economic Analyzer. Process equipment information and stream sizes were taken from the process simulation and entered into the Aspen Process Economic Analyzer were equipment sizes were calculated and information such as materials of construction were added for each piece of equipment. Using these tools the purchase cost for each piece of equipment required was determined along with the utility costs required to run the process. These total cost values were

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[103] A Realistic Look at Hydrogen Price Projections, Doty, http://www.dotynmr.com/PDF/Doty_H2Price.pdf (accessed December 9, 2013)

[104] Yasuo Tanbe; Jun Toriya; Masato Sato; Ken Shiraga; Process For Preparing Tetrahydrofuran. 4093633, June 6, 1978.

[105] Mueller, H.; Palm, C.; Preparation of Tetrahydrofuran. 4588827, May 13, 1986.

[106] Budge, J. R.; Pedersen, E.; Hydrogenation of Maleic Anhydride to Tetrahydrofuran. 4810807, March 7, 1989.

[107] Wood, A.W.; Willet, P.; Colley, S.W.; Shariff, M.; Process For The Purification Of Butane-1,4-diol. 6,137,016, October 24, 2000.

extracted from the software and entered into an in-house economic evaluation to determine the capital investment and the annual operating cost of the THF process from biomass. Tables are provided in the next few pages that show the factors contributing to the total capital cost and annual operating cost.

**Table 8**

**Determination of Capital Requirements of iCARD Process in Pulp Mill Making THF**

| Capital Investment for 32 Million lb.Year THF | | | |
|---|---|---|---|
| Investment | Cost Factor / Basis | | Price |
| Purchased Equipment + Catalyst[1] | Aspen Economic Analysis Result | | $ 2,937,658 |
| Installation | 0.35 | On Purchased Equipment | $ 1,028,180 |
| Instrumentation | 0.10 | On Purchased Equipment | $ 293,766 |
| Piping | 0.15 | On Purchased Equipment | $ 440,649 |
| Electrical | 0.12 | On Purchased Equipment | $ 352,519 |
| Building Improvements | 0.15 | On Purchased Equipment | $ 440,649 |
| Subtotal Direct Costs | Sum Direct Costs | | $ 5,493,420 |
| Engineering & Supervision | 0.15 | On Direct Costs | $ 824,013 |
| Construction & Fee | 0.15 | On Direct Costs | $ 824,013 |
| Contingency | 0.15 | On Direct Costs | $ 824,013 |
| Subtotal Indirect Costs | Sum Indirect Costs | | $ 2,472,039 |
| Fixed Capital Investment | Sum Direct and Indirect Costs | | $ 7,965,460 |
| Working Capital | 0.15 | On Fixed Capital | $ 1,194,819 |
| Total Capital Employed | Sum all Costs | | $ 9,160,279 |

Based on the size of the pre-hydrolysate stream entering the KSE THF process from the mill shown in the previous table the capital cost for the equipment may seem low for the overall process. While the reactive distillation column has to be large to accommodate this flow it rejects the majority of the stream out the bottom. Additionally materials of construction are anticipated to be relatively inexpensive due to benign process conditions after the reactive distillation column. Only the bottom most section of the reactive distillation column are there conditions that warrant more durable materials of construction. This is due to the potential presence of solid materials and continual contact with dilute sulfuric and acetic acid. For these conditions the bottom section of the reactive distillation column is constructed from 316 stainless steel. The rest of the process was estimated based on its construction from carbon steel.

In addition to the attractive capital investment for a THF process of this size, the operating costs of the process are low. The analysis of the annual operating cost was performed in a similar nature to the capital investment cost determination but do not include the raw material costs of the process discussed earlier. The utilities cost taken from the economic analysis software represents the cost to run the process without any resources being provided by the parent mill. This value represents the highest cost estimate on utilities that can be expected for the THF process and an elementary heat integration analysis was done to reduce the primary driver of the utility cost; heat needed to supply the reactive distillation column. It is also anticipated that the pulp mill may have considerable resources available to supply a portion of the heating and electrical requirements to the KSE process. In general the hot water pre-hydrolysate stream is heated under pressure to at least a temperature of 130 °C in the mill for the extraction of the hemicellulose.[108,109] At this temperature the hydrolysate stream could likely be used to run the reboiler of reactive distillation column and ease the energy requirements for other process equipment. An intensive energy optimization however has not been conducted due to the variability of all these factors. For the purpose of estimating the cost of utilities for the KSE process with these considerations in mind 20% of the full utility cost of running the THF was taken from Aspen and used as the utility cost for the KSE process. The utility costs for electric and fuel resources entered into the Aspen Process Economic Analyzer are shown in Table 9.

**Table 9**
**Process Utility Cost Assumptions in iCARD Economic Analysis**

| Process Utility Costs | | |
|---|---|---|
| Cost Of Electricity | $ 0.068 | USD/kWh |
| Cost Of Natural Gas Fuel | $ 4.52 | USD/MMBtu |

These utility values were obtained from the monthly national average cost listings for industrial sector consumption over the past two years.[110,111] Again, 20% of the total utility cost with no heat integration calculated by the economic analyzer was entered and used in the table below to determine the total annual operating cost of the THF process.

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[108] Borrega M., Tolonen, L. K., Bardot F., Testova L., Sixta H.; Potential of hot water extraction of birch wood to produce high-purity dissolving pulp after alkaline pulping. *Bioresource Technology* 2013, 135, 665-671.

[109] Borrega M., Nieminen K., Sixta H.; Degradation kinetics of the main carbohydrates in birch wood during hot water extraction in a batch reactor at elevated temperatures. Bioresource Technology 2011, 102, 10724-10732.

[110] Natural Gas Monthly October 2013; U.S. Energy Information Administration, U.S. Government Printing Office: Washington, DC, 2013.

[111] Electric Power Monthly reports produced by the EIA for the period spanning between the two reports listed:
Electric Power Monthly March 2012 With Data for January 2012; U.S. Energy Information Administration, U.S. Government Printing Office: Washington, DC, 2012.
Electric Power Monthly with Data for September 2013; U.S. Energy Information Administration, U.S. Government Printing Office: Washington, DC, 2013.

**Table 10**
**Annual Operating Costs for iCARD Technology in Pulp Mill to Make THF**

| Annual Operating Costs for 32 Million lb. per Year Plant | | | |
|---|---|---|---|
| Investment | Cost Factor / Basis | | Price |
| Operators | 4 | Number Of Workers/Salary | $ 60,000 |
| Supervisors | 1 | Number Of Workers/Salary | $ 90,000 |
| Operating Labor | 4 | Shifts/Total Annual Cost | $ 960,000 |
| Supervisory Labor | 4 | Shifts/Total Annual Cost | $ 360,000 |
| Maintenance | 0.05 | On Fixed Capital | $ 398,273 |
| Total Utility Costs | 20% Aspen Economic Analysis Result | | $ 1,493,062 |
| Supplies | 0.10 | On Labor | $ 132,000 |
| Plant Laboratory | 0.10 | On Labor | $ 132,000 |
| Depreciation | 0.05 | On Fixed Capital | $ 398,273 |
| Taxes | 0.02 | On Fixed Capital | $ 159,309 |
| Insurance | 0.02 | On Fixed Capital | $ 159,309 |
| Plant Overhead | 0.30 | On Labor & Maintenance | $ 515,482 |
| G&A | 0.15 | On Labor & Maintenance | $ 257,741 |
| Distribution & Sales | 0.05 | On Total Costs Shown Above | $ 248,272 |
| Sales Support: R & D | 1.50 | On Distribution & Sales | $ 372,409 |
| Interest | 0.05 | On Capital Employed | $ 458,014 |
| Total Operating Costs | Sum All Operating Costs | | $ 6,044,144 |

With the total annual operating cost, raw materials cost and capital investment cost determined, the total costs for running the process and the revenue from selling the THF product were calculated and compared. It includes the manufacturing cost of THF based on a capital charge of 25% and the payout time to repay the capital invested based on the profitability after the costs of running the process. Based on this analysis it appears that there is significant economic opportunity for the production of THF based on the KSE technology. Due to the high anticipated profitability of this process it was decided to add to the annual costs a premium payment to the pulp mill for use of their hydrolysate stream on top of the fuel value they were already receiving. This table is shown below.

**Table 11**
**Summary of Economic Performance for iCARD Process in Pulp Mill**

| Annual Project Costs & Revenue For 32 Million lb. per Year | | |
|---|---|---|
| Annual THF Produced | 32,379,910 | lbs |
| THF Market Prices | $ 1.70 | USD/lbs |
| Revenue Generated From Sale Of THF | $ 55,045,847 | USD |
| Fuel Costs To Replace Lost Pentosan | $ 2,141,292 | USD |
| Cost Of Hydrogen Consumed In Reactors | $ 1,675,420 | USD |
| Cost Of Sulfuric Acid Catalyst For Hydrolysate | $ 1,638,936 | USD |
| Net Revenue | $ 49,590,199 | USD |
| Total Process Operating Costs | $ 6,044,144 | USD |
| Premium Paid To Pulp Mill | $ 8,709,211 | USD |
| Profitability After Costs | $ 34,836,843 | USD |
| Capital Charge Rate 1 | 25% | |
| Capital Charge | $ 1,991,365 | USD |
| Manufacturing Cost Of THF | $ 0.686 | USD/lbs |
| Fixed Capital Investment | $ 7,965,460 | USD |
| Payout Period | 0.23 | Years |

In addition to the pulp mill case which is our main interest a smaller toll manufacturing process for THF was built and had the same economic analysis performed. A few key changes were made that affect the annual costs for this process. First, purified furfural in this case is purchased from China and is fed to the process in this form. This change removed the requirement to purchase sulfuric acid and a hydrolysate stream. The second change is that water had to be added to this process to retain the functionality of the reactive distillation column. Retaining the reactive distillation column however provides the unique separation properties of the system and the opportunity to make sure it functions as designed in the simulations. Table 10, shown below includes the process costs and stream requirements needed to run the 3 million pound per year toll manufacturing process. The cost of natural gas and electricity were shown in Table 10.

**Table 12**
**Toll Manufacturing Stream Flow Rates and Commodity Costs**

| Basis for Cost Estimation | | |
|---|---|---|
| Item | Amount | Units |
| THF Produced Annually | 3,113,017 | lbs/yr |
| Furfural Consumed In Process | 4,285,786 | lbs/yr |
| Hydrogen Consumed In Process | 178,289 | lbs/yr |
| Cost Of Furfural | $ 0.45 | USD/lbs |
| Cost Of Hydrogen | $ 0.91 | USD/lbs |

Analogous to the pulp mill economic analysis, the determination for the toll manufacturing capital costs and annual costs are shown below in tables 11 and 12 respectively.

### Table 13
### Toll Manufacturing iCARD Technology Capital Investment *IF* Toll Plant Were New Investment[112]

| Capital Investment | | | |
|---|---|---|---|
| Investment | Cost Factor / Basis | | Price |
| Purchased Equipment + Catalyst (1) | Aspen Economic Analysis Result | | $ 530,686 |
| Installation | 0.35 | On Purchased Equipment | $ 185,740 |
| Instrumentation | 0.10 | On Purchased Equipment | $ 53,069 |
| Piping | 0.15 | On Purchased Equipment | $ 79,603 |
| Electrical | 0.12 | On Purchased Equipment | $ 63,682 |
| Building Improvements | 0.15 | On Purchased Equipment | $ 79,603 |
| Subtotal Direct Costs | Sum Direct Costs | | $ 992,382 |
| Engineering & Supervision | 0.15 | On Direct Costs | $ 148,857 |
| Construction & Fee | 0.15 | On Direct Costs | $ 148,857 |
| Contingency | 0.15 | On Direct Costs | $ 148,857 |
| Subtotal Indirect Costs | Sum Indirect Costs | | $ 446,572 |
| Fixed Capital Investment | Sum Direct and Indirect Costs | | $ 1,438,955 |
| Working Capital | 0.15 | On Fixed Capital | $ 215,843 |
| Total Capital Employed | Sum all Costs | | $ 1,654,798 |

### Table 14
### Toll Manufacturing THF Process Annual Operating Costs

| Annual Operating Costs | | | |
|---|---|---|---|
| Investment | Cost Factor / Basis | | Price |
| Operators | 2 | Number Of Workers/Salary | $ 60,000 |
| Supervisors | 0.5 | Number Of Workers/Salary | $ 90,000 |
| Operating Labor | 4 | Shifts/Total Annual Cost | $ 480,000 |
| Supervisory Labor | 4 | Shifts/Total Annual Cost | $ 180,000 |
| Maintenance | 0.05 | On Fixed Capital | $ 71,948 |
| Total Utility Costs | 20% Aspen Economic Analysis Result | | $ 144,466 |
| Supplies | 0.10 | On Labor | $ 66,000 |
| Plant Laboratory | 0.10 | On Labor | $ 66,000 |
| Depreciation | 0.05 | On Fixed Capital | $ 71,948 |
| Taxes | 0.02 | On Fixed Capital | $ 28,779 |
| Insurance | 0.02 | On Fixed Capital | $ 28,779 |
| Plant Overhead | 0.30 | On Labor & Maintenance | $ 219,584 |
| G&A | 0.15 | On Labor & Maintenance | $ 109,792 |
| Distribution & Sales | 0.05 | On Total Costs Shown Above | $ 73,365 |
| Sales Support: R & D | 1.50 | On Distribution & Sales | $ 110,047 |
| Interest | 0.05 | On Capital Employed | $ 82,740 |
| Total Operating Costs | Sum All Operating Costs | | $ 1,733,448 |

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[112] The Toll Processing Plant exists today, and would require $S85,000 to upgrade for use with iCARD technology. The estimates shown are for the hypothetical case that a new Toll Processing Plant were built, in order to exemplify the economic statistics had the Plant been built new at the same capacity as the existing Toll Processing Plant.

Again a total analysis was done on the economics of the toll manufacturing plant to determine the manufacturing costs of THF and the payout time for a small plant. This analysis is shown below in Table 13.

**Table 15**
**Annual Project Costs & Revenue for the Toll Manufacturing Case**

| Annual Project Costs & Revenue For The Pulp Mill Case | | |
|---|---:|---|
| Annual THF Produced | 3,113,017 | lbs |
| THF Market Prices | $ 1.70 | USD/lbs |
| Revenue Generated From Sale Of THF | $ 5,292,128 | USD |
| Cost Of Furfural Feed Stock | $ 1,928,604 | USD |
| Cost Of Hydrogen Consumed In Reactors | $ 161,741 | USD |
| Net Revenue | $ 3,201,784 | USD |
| Total Process Operating Costs | $ 1,733,448 | USD |
| Profitability After Costs | $ 1,468,336 | USD |
| Capital Charge Rate | 25% | |
| Capital Charge | $ 359,739 | USD |
| Manufacturing Cost Of THF | $ 1.344 | USD/lbs |
| Fixed Capital Investment | $ 1,438,955 | USD |
| Payout Period | 0.98 | Years |

A key difference between the analysis in Table 13 and the one performed on the pulp mill in Table 9 is the removal of the premium payment. While still profitable as a small process the margin between the process costs and the profitability is much smaller compared to the large process utilizing a cheap feed stock. A final comparison Table 17, is included below to compare side by side the economics of the 3 million pound per year toll manufacturing case[113] and the 32 million pound per year pulp mill case.

**Table 16**
**Process Economic Comparison between Plant Sizes**

| | | 3 Million PPY Case | 32 Million PPY Case |
|---|---|---:|---:|
| Fixed Capital Investment | (USD) | 1,438,955 | 7,965,460 |
| Capital Charge Rate | | 25% | 25% |
| Capital Charge | (Per lbs THF) | $ 0.116 | $ 0.062 |
| Total Feed Costs | (Per lbs THF) | $ 0.671 | $ 0.168 |
| Total Process Operating Costs | (Per lbs THF) | $ 0557 | $ 0.456 |
| Manufacturing Cost of THF | (Per lbs THF) | $ 1.344 | $ 0.686 |
| THF Sale Price | (USD/lbs) | $ 1.700 | $ 1.700 |
| Payout Period | (Years) | 0.98 | 0.23 |

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[113] The capital investment shown in Table 16 for the 3 million pound year plant is for informational purposes only, to illustrate economic performance based on the hypothetical cost of an entirely new plant. However, in this program, we have set aside $85,000 (see Commercialization Plan) for conversion of an existing toll processing facility for use in this case.