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Techno-economic analysis of 5-nonanone production from levulinic acid

Akshay D. Patel [a], Juan Carlos Serrano-Ruiz [b], James A. Dumesic [b], Robert P. Anex [a,*]

[a] *Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA 50011, United States*
[b] *Department of Chemical and Biological Engineering, University of Wisconsin, 1413 Engineering Drive, Madison, WI 53706, United States*

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ABSTRACT

We analyze a process for production of 5-nonanone (dibutyl ketone, DBK) from levulinic acid (LA) which is a biobased platform chemical that can be produced in large quantities from a variety of lignocellulosic biomass sources. The techno-economic analysis is based on a catalytic pathway developed in lab scale. The final product (DBK) has applications as an industrial solvent and serves as a platform chemical for the production of liquid hydrocarbon fuels in the diesel and gasoline ranges. A detailed process model has been created for two different product purity levels (90% and 99%). Process economics have been studied in a discounted cash flow analysis to analyze the viability of production and relative product purification costs. The modeled process utilizes 480 metric ton/day of LA feedstock to produce 194 metric ton/day of DBK along with other by-products. Sensitivity analysis is used to identify the impact of key parameters on the minimum selling price of product. Thus, the price of the feedstock (LA) and the DBK final yield were found to be the most sensitive parameters affecting the final price of the product. With the current LA market price ($3.2 per kg) and the experimental yield of 66%, the minimum selling price estimated for a high purity DBK was $8.5 per kg, comparable to the current DBK purchase price ($9.07 per kg) but still quite high compared to the price of a typical petroleum-derived solvent such as methyl ethyl ketone ($0.77 per kg). Further improvements on the lab scale to increase the yield of DBK, and the use of inexpensive LA from the patented Biofine process, would allow the production of DBK at competitive prices for chemical and fuel applications.

1. Introduction

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

The analysis described herein involves a process to produce 5-nonanone (dibutyl ketone, DBK) from concentrated aqueous solutions of levulinic acid (LA). LA is a platform chemical which can be obtained from a wide range of cellulosic biomass feedstocks including wastes [5,7]. Large scale production of LA from biomass is possible through a currently well-established patented technology [8]. By means of this process, LA can be produced at low price of $0.09–$0.22 per kg ($0.04–$0.10 per pound), thus enabling its use as platform molecule for the production of other important chemicals such as methyl-tetrahydrofuran (MTHF, an important fuel additive), δ-aminolevulinic acid (DALA, a biodegradable insecticide) [5] and, in the case of the present paper, DBK. DBK is an important industrial solvent with applications in paints, resins and a variety of other areas [9]. Additionally, DBK can also potentially serve as platform molecule for the production of liquid hydrocarbon fuels for the transportation sector [10].

The process described herein involves the catalytic processing of LA to DBK in two steps [10]. In the first step, LA (in form of an aqueous solution) is almost quantitatively reduced under H_2 over a Ru/C catalyst to yield γ-valerolactone (GVL). In the second step, this GVL product is ring-opened and hydrogenated over a bifunctional (metal and acid sites) Pd/Nb_2O_5 to produce pentanoic acid, a

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Abbreviations: DBK, 5-nonanone dibutyl ketone; LA, levulinic acid; MEK, methyl ethyl ketone; MSP, minimum selling price.

* Corresponding author at: 3202 NSRIC Building, Ag & Biosystems Engineering, Iowa State University, Ames, IA 50011, United States. Tel.: +1 515 294 6576; fax: +1 515 294 4250.
E-mail address: rpanex@iastate.edu (R.P. Anex).

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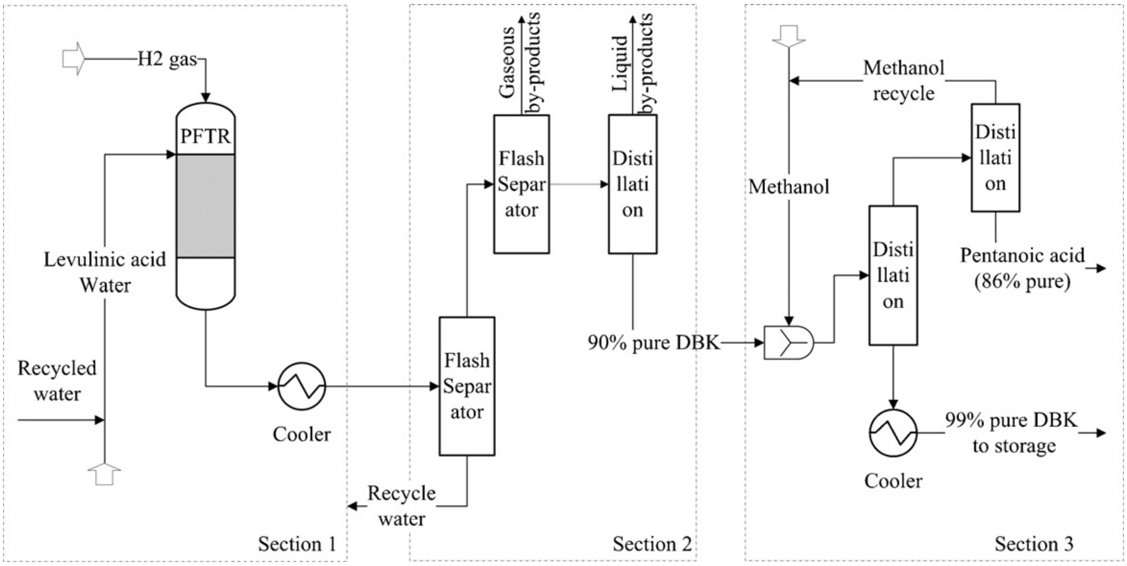

Fig. 1. Flow diagrams for the process of production of DBK from levulinic acid.

reaction intermediate that can be upgraded to DBK over the same Pd/Nb_2O_5 bed. We note that these two steps can be carried out in a single reactor by using a dual catalyst bed ($RuC + Pd/Nb_2O_5$) in a cascade arrangement, allowing the direct production of an organic stream enriched in DBK that spontaneously separates from water. As a part of this analysis, we have carried out simulation of this route and the subsequent purification steps. The process has been modeled to utilize 480 metric ton/day of LA which is based on the assumption of a 2000 metric ton/day biomass refinery facility producing LA [8]. This case leads to the production of DBK along with a mixture of hexanone, heptanone, n-nonane, n-butane and pentanoic acid as by-products [10]. The high scale approach allowed us to evaluate possible fuel and large scale chemical applications for DBK. With the exception of pentanoic acid, the rest of by-products and gases are relatively easily separated from the product stream, while the separation of pentanoic acid requires significant further processing. Hence, two scenarios have been modeled, one with 90% product purity and other with >99% product purity (chemical grade) to evaluate the costs and benefits involved in further purifying the product for its use as a chemical.

2. Materials and methods

The modeled process uses 480 metric ton/day LA which undergoes catalytic processing to yield DBK along with other by-products. The models are steady state process simulations. Actual lab scale data (reaction conditions, product composition, yields, catalyst, and reactor information) were used in the analysis. The production and purification process was modeled using ASPEN Plus process engineering software [11]. Two models were created. The first model involves processing in the reactor and less rigorous purification resulting in 90% pure DBK (pentanoic acid being the major impurity). The second model involves further purification leading to a product with >99% purity. The models are referred to as model ‘A’ (90% purity) and model ‘B’ (>99% purity) throughout the analysis. Laboratory data were used to size the reactor while data from the Aspen model were used to size rest of the process equipment. The results from Aspen model were imported into MS Excel [12] which was used to create an engineering economic model. A discounted cash flow analysis at a set internal rate of return was carried out to arrive at a Minimum Selling Price (MSP) for DBK with a net present project value of zero. This analysis has been carried out with 2007 US Dollar value as a point of reference. The models have been constructed to update all cost values accordingly based on relevant indices. The two process models are at the same scale and differ mainly in the presence of additional purification processes on the front end of the reaction and initial separation steps. Fig. 1 shows the process flow diagram. Sections 1 and 2 are common to both the models, while Section 3 involves further purification process to produce pure DBK and is present only in model ‘B’. Detailed process flow diagrams can be found in Appendices A–D.

2.1. Production process

Section 1 (Fig. 1) involves feed mixing and reaction. LA and hydrogen gas are the major raw materials required for the process. A 50 wt% solution of LA in water is fed to the reactor along with hydrogen gas. In a plug flow tubular reactor LA reacts to yield DBK, CO_2 and water, as indicated in reaction (1):

$$2C_5H_8O_3 + 4H_2 \rightarrow C_9H_{18}O + CO_2 + 3H_2O \quad (1)$$

The catalyst beds are operated at 350 °C, 3.44 MPa pressure and a weight hourly space velocity (WHSV, defined as mass of LA fed per hour/mass of catalyst used) of $1\,h^{-1}$. 100% of the LA fed is converted in the reactor. The overall reaction produces DBK as the main product, with 2-heptanone, 3-hexanone, n-nonane, n-butane and pentanoic acid being the by-products of the process. Water, unreacted hydrogen and carbon dioxide are present in the reactor output along with the product and by-products.

In Section 2 (Fig. 1), the reactor output stream is cooled and flashed to separate water which is recycled after purging. The remaining stream is flashed again at a lower temperature and pressure to separate the gaseous by-products which mainly include carbon dioxide, unreacted hydrogen and butane gas. The liquid output from the second flash is subjected to distillation to separate the remaining by-products. The liquid distillate, which forms the liquid by-product stream, consists of a mixture of 2-heptanone, 3-hexanone, n-butane, n-nonane and small amounts of pentanoic acid. The liquid obtained downstream includes DBK with 90% purity, with pentanoic acid (9.2%) and other components present in trace quantities accounting for the rest of products. In case of model ‘A’, the bottoms product is the final product stream which is cooled and sent to storage. Alternatively, the liquid obtained from Section 2 can be further purified in Section 3 (model ‘B’). The overlapping boiling points of DBK and pentanoic acid prevented the utilization of direct distillation techniques for DBK purification. Instead, and after simulations with a wide range of polar solvents, extraction with methanol was chosen to aid the separation process. Methanol is then mixed with the impure DBK stream from Section 2, and the resulting stream is passed through a series of distillation columns which are sequenced so that the bottoms product from each is 99% pure DBK and the distillate is fed to the following column. This strategy allows the recovery of 98% of the methanol from the pentanoic acid by-product at the end of separation sequence, and 4% is purged out before recycle. As a result, pentanoic acid can be be obtained with 87% purity as a by-product while the pure DBK streams are mixed and cooled before being sent to storage.

2.2. Economic model and key assumptions

A discounted cash flow analysis is used to assess the process economics which are modeled using an Excel spreadsheet following the NREL model [12]. The stream data for material, heat and work streams are imported into the spreadsheet from Aspen model. The process equipment was sized using standard procedures [13]. The purchased equipment cost (PEC) was estimated using data from Peters and Timmerhaus [13], NREL Ethanol design report 2001 [12] and ICARUS process evaluator [14]. Total installed equipment cost (TIC) and indirect plant expenses have been set as fractions of purchased equipment cost. Installation costs include charges for equipment installation, instrumentation, piping, electrical connections, building, warehouse and site development. Indirect expenses include costs for engineering and supervision, construction expenses, legal and contractor fees. Contingency cost is estimated as 20% of the total direct and indirect plant costs. The total direct and indirect costs along with the contingency give an estimate of the fixed capital investment (FCI) required for the project. Working capital accounts for the startup costs and is estimated as 15% of FCI. The FCI and working capital constitute the total capital investment (TCI) in the project. The prices for feedstock, raw materials and by-products have been derived from market data and conservative estimates based on assumptions. It is assumed that utilities required for the plant are purchased and the wastewater treatment is carried out for a fixed price at an external facility. Labor costs are estimated based on general assumptions for employee hours required per day for the number of operating steps. Overhead expenses are accounted as a fraction of labor costs and maintenance costs are calculated as a fraction of the total purchased equipment cost. Insurance and legal fees are calculated as a fraction of installed equipment costs. These costs comprise the operating costs for the process. The total purchase cost of catalyst is incurred at every 10-year intervals in the discounted cash flow analysis. Currently it is priced at $4000 per kg.

The discounted cash flow analysis is based on certain assumptions and takes into account cash flows over the entire plant life. In the discounted cash flow analysis the project investment is spent over three years following the assumptions stated below. The total operating costs are incurred every year and also include credit from sale of co-products. The catalyst costs are incurred at fixed intervals following the assumptions. The plant depreciation costs are recovered in the first seven years of operation following MACRS method. The annual sales of DBK follow the selling price in $/kg and annual plant output from the process. The difference between these annual costs and the annual sales of DBK give the net revenue in the respective year. Income tax is incurred at the rate of 39% on the taxable income derived after covering the losses forwarded from the previous operating year. Deducting the income tax from the net revenue gives us the annual cash income for each operating year. These revenue streams from the operating years and the investment costs are discounted to the 2007 year of reference following a 10% internal rate of return. The sum of these costs and revenues in the year of reference give us the net present value (NPV) of the project. In the current analysis the selling price of DBK is iterated at a set internal rate of return to gain a net project value of zero. This DBK price at zero net present value is the Minimum DBK Selling Price (MSP). The following items are some of the major assumptions critical to the analysis.

- The process has been modeled to utilize 480 metric ton/day of LA which is assumed to be produced from processing 2000 metric ton/day cellulosic biomass through the Biofine process [15].
- The detailed reaction kinetics are unknown and hence experimental yields are used in analysis. The reactor size is estimated using residence time and catalyst bulk density.
- The plant operates on a continuous basis for 8400 h every year.
- This analysis assumes an *n*th plant being built. The risk of unforeseen expenses incurred in setting up of a pioneer plant based on new process technology, has not been included in this analysis
- The LA feedstock price is assumed to be $3.21 per kg [16]. However, based on Biofine technology, substantial lower prices for LA are possible, and this possibility will be taken into account.
- The plant is 100% equity financed and the lifetime is assumed to be 20 years.
- The construction period is assumed to be 3 years, with 32% of the capital investment spent in 1st year, 60% in year 2 and 8% in year 3.
- The start-up time is assumed to be 6 months during which period the revenues have been assumed to be 50% of normal capacity and the variable costs are assumed to be 75% of normal plant capacity.
- The income tax rate has been assumed to be 39% and the plant is depreciated following the IRS Modified Accelerated Cost Recovery System (MACRS).
- The catalyst has a salvage value at the end of lifetime, which is recovered.
- The Internal Rate of Return (IRR) for this project is set at 10%.
- All the costs and prices are updated to 2007 dollar value using appropriate indices.

3. Results and discussion

3.1. Process analysis

The steady state flow rates of raw materials, product and by-products streams are summarized in Table 1 (detailed flow diagrams for both processes, key stream results and costs of chemicals, as well as the summary of the results from process engineering model are included in Appendices A–D). Both simulated processes described above use a 480 metric ton/day stream of pure LA as feedstock, resulting in production of 215 metric ton/day of 90% purity DBK (model 'A') and 194 metric ton/day of high purity DBK (model 'B'). As a result of LA processing, a liquid by-product stream of 55 metric ton/day is produced, mostly composed of n-nonane (with application as diesel blender agent) and ketones in the C_6–C_7 range (Table 1). The gaseous by-products include about 15% unreacted hydrogen, 79% carbon dioxide and 6% butane. Even though in this analysis this stream is treated as a by-product with low value, an attempt can be made to separate hydrogen and butane from the mixture, allowing the recycle of the unreacted H_2 to the main reactor and the use of butane for the generation of heat required for the process. The CO_2-enriched stream obtained after the separation unit could then be potentially used in applications like algae growth for the purpose of lipids production [17]. Alternatively, the gaseous by-product stream could be used, without the need of separation, for the production of methanol (necessary for the extraction strategy of Section 3, Fig. 1) by means of catalytic hydrogenation of

Table 1
Mass flow rates of key components of 2 modeled processes for DBK production from LA.

	Model 'A' (90% purity) (metric ton/day)	Model 'B' (>99% purity) (metric ton/day)
Raw materials		
Levulinic acid	480	480
Water	156	33
Hydrogen gas	41.6	41.6
Methanol	–	1.5
DBK production	215	194
DBK	195	193
Impurities	20 (Pentanoic acid)	1
Liquid by-product stream	55	55
3-Hexanone	27	27
2-Heptanone	10	10
Nonane	11	11
Butane	4	4
Pentanoic acid	1.3	1.3
Gaseous by-products	173	173
Hydrogen	25	25
Carbon-di-oxide	136	136
Butane	11	11
Pentanoic acid stream	–	22
Pentanoic acid	–	19
DBK	–	2

CO_2 [18] using the remnant hydrogen from the DBK processing. All these improvements in the process can result in a more favorable economic analysis. In case of model 'B' an extra purification step is used to purify DBK, leading to the production of a 22 metric ton/day stream of pentanoic acid with 86% purity. This product can be further purified for applications in a wide variety of areas including lubricants, plasticizers, and pharmaceuticals [19].

3.2. Economic analysis

The capital expenses for the production of DBK from LA are summarized in Table 2 (a more detailed list of capital expenses for each processing unit can be found in Appendices A–D). Section 1 accounts for a large fraction of the total installed costs, with the reactor representing the major expense in this sense (75% of total installed cost for model 'A' and 57% of total installed cost for model 'B'). As expected, model 'B' requires an excess of $6.4 million in total capital investment mainly due to the increased capital requirements for additional purification section.

The operating expenses are included in Table 3. The cost of the feed LA is a major contributor to the operating expenses that accounts for 97% of the total operating costs. As will be discussed below, the price of LA is a crucial factor determining the economic feasibility of the process. The utility costs are higher in case of model 'B' due to the additional requirement in the purification area. However, a higher by-product credit is obtained in this case due to the separation of pentanoic acid, which can be sold separately at a higher price than the mixed by-product stream.

Table 2
Capital expenses for the production of DBK from LA.

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

Table 3
Operating expenses for the production of DBK from LA.

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

Table 4 shows the final results from the discounted cash flow analysis, including the MSP of DBK for both models. The higher DBK production and yield in model 'A' is mainly due to the presence of impurities in the product stream, since loss of DBK product in purification is minimal. For model 'B', an LA input of 168,000 metric ton/year produces 68,035 metric ton/year of high purity DBK. This scale is reasonable for solvent applications, when compared with methyl ethyl ketone (MEK), which is expected to have a worldwide market demand of 1.3 million metric ton by 2010 [20]. The product yield is 405 kg/metric ton of LA, which is at 98% of the experimental yields and about 66% of the stoichiometric yields. This result shows that the losses in purification process are minimal. The total capital investment for this project is estimated to be $31.7 million. The present value of catalyst cost at $198 million over the entire plant life is significantly higher as compared to the total capital investment in the project. About 40 metric ton of catalyst priced at $4000 per kg is needed to maintain continuous production at the modeled scale. Thus, research to identify new inexpensive materials as catalysts seems to be important to ensure economic feasibility of the process.

The MSP for DBK is higher (by 15%) in case of model 'B' since a higher purity product is obtained and can justify its price. Importantly, the cost of LA feed is the major factor influencing MSP and the overall project feasibility. The MSP for a high purity DBK was found to be $8.49 per kg, which is comparable to the current DBK purchase price ($9.07 per kg) [21]. However, for large scale solvent applications similar to MEK, the price is quite high when compared to MEK price of $0.77 per kg [22].

3.3. Sensitivity analysis

Process and economic sensitivity analyses have been performed to gauge the impact of variations in key parameters on the MSP, and results are shown in Fig. 2 for model 'B'. The values for these parameters are based on experimental data or assumptions. Based on our confidence in the assumed values, we have studied the effect of 20% variation in these parameters on the MSP of DBK. This analysis helps in identification of key bottlenecks and provides a direction

Table 4
Results of discounted cash flow analysis.

	Model 'A'	Model 'B'
Annual LA input (metric ton/year)	168,000	168,000
Annual DBK production (metric ton/year)	75,452	68,035
Product yield (kg/metric ton feed)	450	405
Total capital investment (million USD)	25.3	31.7
Catalyst cost (million USD)[a]	197.7	197.7
Minimum product selling price ($/kg)	7.70	8.49
Minimum product selling price ($/l)	6.35	6.92

[a] Present value over project lifetime.

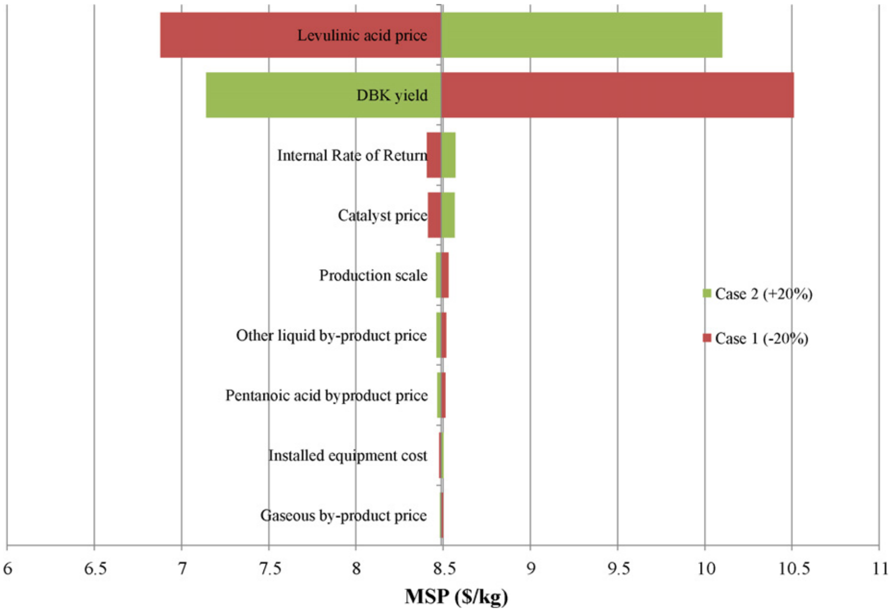

Fig. 2. Sensitivity analysis of change in MSP for several parameters.

for future development in this process. As can be seen, the feedstock price and the DBK yield are, by far, the two parameters most affecting the MSP, with the catalyst price and the credit obtained from by-products having less impact on the economics of the process.

3.4. Bottlenecks and possible approaches

Fig. 2 shows that the process is most sensitive to the price of LA feedstock. Thus, a 20% change in the price of feedstock results in about 19% change in the MSP. A price quote of $3.21 per kg [16] is used for base case. The price and availability of LA is a major bottleneck in implementation of this process. The Biofine process designed by Biometics, LLC promises LA production from waste cellulosic biomass at a price of about $0.09–$0.22 per kg [5] when produced on a sufficiently large scale. Commercial availability of LA in large quantities at these low prices can result in a MSP for DBK in the range of $0.69–$0.99 per kg which represents approximately 90% reduction. Such low prices would enable the use of DBK as a commodity scale solvent. However the commercial status of this process is not known. Additionally the economics for ethyl levulinate production following LA from the Biofine process [8] assume a price of $40 per metric ton ($36 per short ton) for biomass which will be subject to change based on the demand for biomass. At this price for biomass although the higher LA price of $0.22 may be plausible, the lower price target of $0.09 per kg seems difficult to attain. Using the economics for Ethyl levulinate production from Ref. [8], an approximate analysis has been performed based on 5% change in values for relevant production and capital costs to extract the price for LA. Two scenarios emanate from this analysis. In the first scenario we assume that the capital cost is evenly spread over a plant life of 20 years. In this scenario adding up the annual processing costs and capital costs, results in a LA price of $0.25/kg. This price is fairly close to the $0.22 upper range for LA from Ref. [6]. In the second scenario a discounted cash flow analysis has been performed, similar to the one used for DBK analysis. A 10% IRR, 20 year plant life and NPV = 0 results in a LA price of $0.34/kg which is 1.5 times higher than the $0.22/kg upper range presented earlier. LA at $0.34/kg results in a DBK price of $1.29/kg. This still represents about 85% reduction in the MSP for DBK, but makes DBK 1.7 times more expensive as compared to MEK. However with improvements in the process for production of LA one can expect lower prices for LA in future.

The other important parameter affecting the MSP in our process is the DBK total yield. Fig. 2 shows that a 20% increase in overall DBK yield, accompanied by a decrease in by-product yields, can decrease the MSP by 16% to $7.1/kg. As modeled, the current process yields are approximately 98% of the experimental yields (there are minor losses in the purification of DBK) and thus the yield of DBK in the reactor is a major bottleneck that needs to be targeted. A 20% increase in the reaction yield of DBK can reduce the MSP by 14% to $7.3/kg. Also the stoichiometric yield of DBK through this pathway is 612 kg/metric ton and the current process yield is 66% of this maximum. Increase in yields can be possible through improvements in catalyst and optimizing reaction conditions. These improvements would lead to an increase in production of DBK while decreasing by-product formation.

To illustrate the effect of increase in yields, we have carried out calculations for the case where the yield of DBK is equal to 85%, with no pentanoic acid in product and only easily separable hexanone and heptanone. This situation corresponds to the best yield that we have achieved in the laboratory using an additional bed of ceria–zirconia in a cascade arrangement. In this new configuration, the conditions in the first bed are adjusted to produce the intermediate pentanoic acid with high yields, whereas the second bed of ceria–zirconia achieves ketonization of pentanoic acid to DBK [10]. As a result, DBK is obtained free of pentanoic acid as a high-purity organic stream that spontaneously separates from water. This case eliminates the need for extra purification, thus reducing capital and operating costs. This high yield process results in a 21% lower MSP for DBK of $6.68/kg at a LA price of $3.21/kg. For a LA price of $0.09–$0.22/kg from the Biofine process, a low DBK MSP of $0.59–$0.85 would be possible, which could certainly increase the competitiveness of DBK as compared to other commodity scale solvents like methyl ethyl ketone. Additionally, the organic stream could be used to produce fuels (diesel and gasoline) in an additional reactor [10], and we anticipate that the use of inexpensive LA from the Biofine process would allow the production of Diesel and gasoline at competitive prices ($0.5–$0.8/l) ($2–$3 per gallon), leading to a promising approach for fuels production from biomass.

Even with maximum theoretical yields, the current price of LA corresponds to a MSP of \$5.81/kg. If LA can be purchased for \$0.22/kg, as projected from the Biofine process, a MSP of \$0.79/kg for pure DBK would be possible with maximum yields. Hence, it is evident that only at low LA feedstock price would DBK be able to compete with MEK which sells for \$0.77/kg [22].

Degradation, deactivation and regeneration studies have not yet been carried out for the catalysts. In such a case there is a significant uncertainty surrounding catalyst requirement and price. A 20% variation in catalyst price under the current assumption, leads to a 1% change in MSP. The catalyst life may be shorter due to faster degradation. In such a case the MSP can rise rapidly due to the increase in the present value of catalyst cost over project lifetime. This behavior also increases the dependency of MSP on catalyst price. With higher rate of catalyst deactivation, more than two reactors might be needed to maintain continuous production. Introduction of an additional reactor over the two reactors can increase the MSP by 2.5% and the total capital investment by 28.4%.

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

The by-products from this process are in the form of a mixed stream. These species need to be separated and purified further to obtain a higher value for the by-products. This purification has not been modeled here. Hence a lower value for the by-product streams is assumed. The higher price that can be obtained for purified by-products would need to justify the additional capital and operating expenses and also subsidize the DBK product price. Given the market price and utility of the by-products, there is a good chance that the MSP for DBK would be reduced in such a case.

4. Conclusions

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

As modeled, the MSP of DBK produced is comparable to its current price. Lower LA price can make DBK an economically attractive solvent. However, at the 2009 quoted price of LA, the MSP is high when compared with prices for other extensively used petroleum-based ketone solvents like methyl ethyl ketone (\$0.77/kg). Nonetheless, with large scale availability of low price LA from the Biofine process and increased yields, it will be possible for DBK to compete on a price basis with solvents like MEK. In such a case, DBK can provide a viable alternative to commodity scale petroleum-based solvents.

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

Overall, the process described here appears to be feasible for the production of DBK as an industrial chemical. The process could be implemented in a biorefinery complex to enable optimum utilization of feedstock based on market demand. It would also enable utilization of by-products in other processes or allow by-products to be sold as biobased industrial chemicals. The feasibility of commodity scale solvent and fuel applications by conversion to alkanes through hydrogenation is mainly dependent on the large scale availability of hydrogen and inexpensive LA.

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Appendix A. Process flow diagram

A.1. Model 'A'

Fig. A.1

A.2. Model 'B'

Fig. A.2

Appendix B. Mass flows and costs for key components

B.1. Model 'A'

Table B1

B.2. Model 'B'

Table B2

B.3. Cost of chemicals

Table B3

Appendix C. List of equipment and cost estimates

C.1. Model 'A'

Table C1

C.2. Model 'B'

Table C2

Appendix D. Summaries of process engineering analysis

D.1. Model 'A'

Table D1

D.2. Model 'B'

Table D2

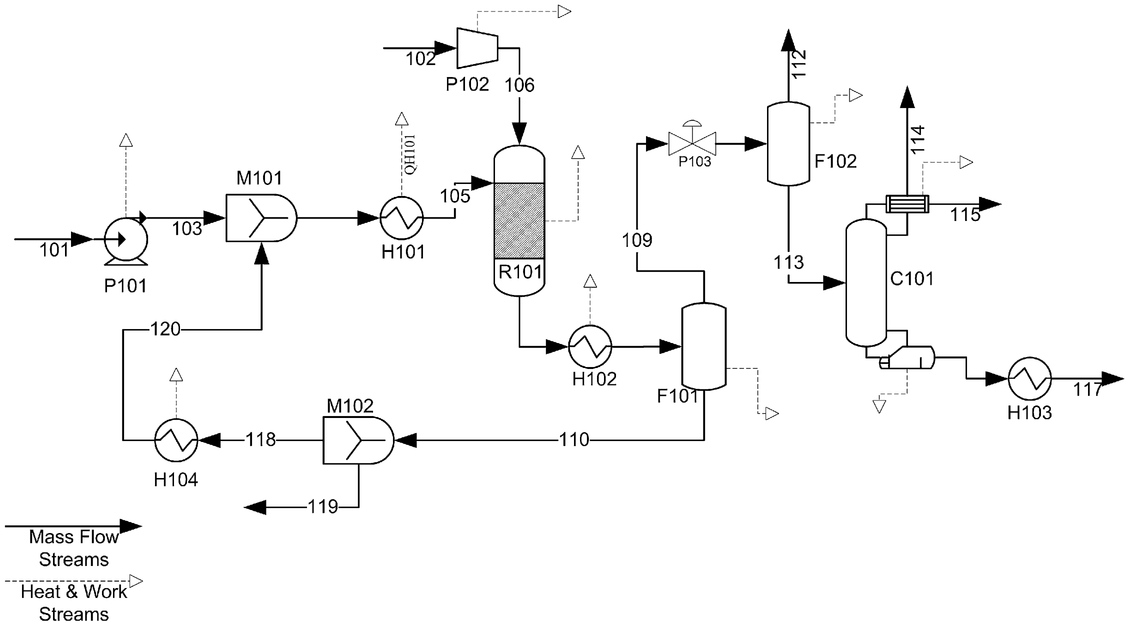

Fig. A.1. Process flow diagram for model 'A' (90% purity).

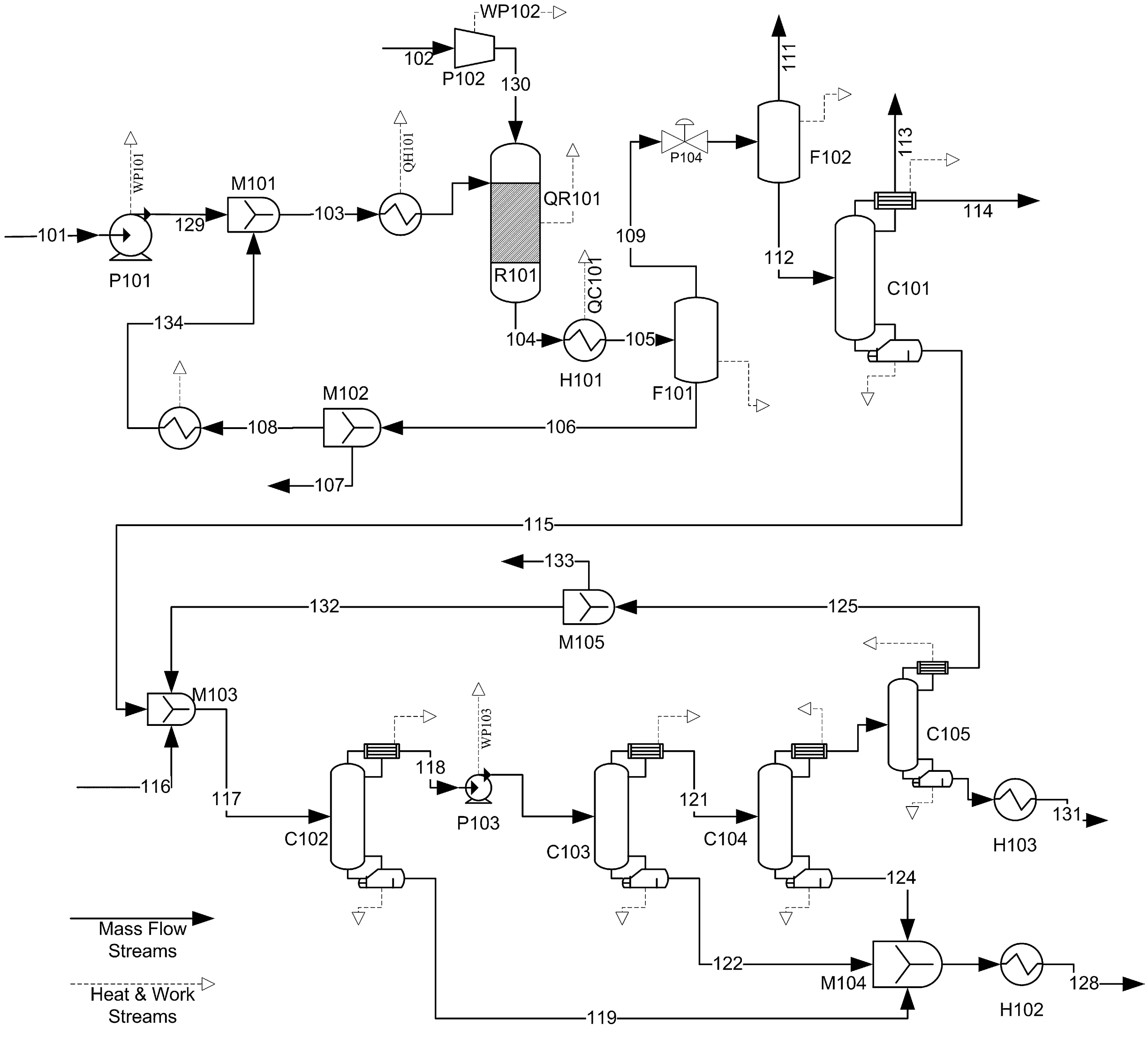

Fig. A.2. Process flow diagram for model 'B' (>99% purity).

Table B1
Mass flow and properties of key streams for model ‘A’.

		Raw material input		Reactor product	Gaseous by-products	
Stream		101	102	107	112	114
Component mass flow						
Levulinic acid	kg/h	20,000	0	0	0	0
Hydrogen	kg/h	0	1736.07	1035.12	1034.2	0.9
Water	kg/h	6512.27	0	23,281.75	13.48	1.57
CO_2	kg/h	0	0	5684.79	5500.12	148
Dibutyl ketone	kg/h	0	0	8168.23	10.59	0
3-Hexanone	kg/h	0	0	1151.98	25.81	3.52
2-Heptanone	kg/h	0	0	417.39	3	0.4
Nonane	kg/h	0	0	492.51	4.17	0.58
Butane	kg/h	0	0	626.08	418.84	46.1
Valeric acid	kg/h	0	0	880.68	0.81	0.01
Mole flow	kmol/h	533.73	861.2	2030.8	646.35	4.73
Mass flow	kg/h	26512.3	1736.07	41,738.52	7011.02	201
Volume flow	L/min	416.51	178,694	49199.01	22,725.1	819
Temperature	K	293.15	303.15	623.15	308.15	308
Pressure	atm	2	2	34.02	12	2.4
Mass density	g/cm^3	1.06	0	0.01	0.01	0

		Liquid by-products	Waste	Product
Stream		115	119	117
Component mass flow				
Levulinic acid	kg/h	0	0	0
Hydrogen	kg/h	0.01	0.01	0
Water	kg/h	11.98	9767	0
CO_2	kg/h	32.66	1.67	0
Dibutyl Ketone	kg/h	26.25	0	8131.4
3-Hexanone	kg/h	1122.33	0	0.33
2-Heptanone	kg/h	399.86	0	14.14
Nonane	kg/h	475.01	0	12.75
Butane	kg/h	161.13	0	0
Valeric acid	kg/h	55.68	0.09	823.97
Mole flow	kmol/h	23.32	542.19	65.46
Mass flow	kg/h	2284.9	9768.8	8982.6
Volume flow	L/min	50	165.41	181.44
Temperature	K	308.15	308.15	303.15
Pressure	atm	2.4	34	1
Mass density	g/cm^3	0.76	0.98	0.83

Table B2
Mass flow and properties of key streams for model ‘B’.

		Raw material inputs			Reactor product	Gaseous by-products	
Stream		101	102	116	104	111	113
Component mass flow							
Levulinic acid	kg/h	20,000	0	0	0	0	0
Hydrogen	kg/h	0	1736.07	0	1035.14	1034.22	0.9
Water	kg/h	1397.32	0	0	23,282.26	13.48	1.57
CO_2	kg/h	0	0	0	5684.91	5500.24	148
Dibutyl ketone	kg/h	0	0	0	8168.41	10.59	0
3-Hexanone	kg/h	0	0	0	1152.01	25.81	3.52
2-Heptanone	kg/h	0	0	0	417.39	3	0.4
Nonane	kg/h	0	0	0	492.53	4.17	0.58
Butane	kg/h	0	0	0	626.09	418.85	46.11
Valeric acid	kg/h	0	0	0	880.7	0.81	0.01
Methanol	kg/h	0	0	58.93	0	0	0
Mole flow	kmol/h	249.8	861.2	1.84	2030.85	646.37	4.73
Mass flow	kg/h	21,397.3	1736.07	58.93	41,739.45	7011.17	201.1
Volume flow	L/min	323.14	178,694	1.25	49,200.11	22,725.6	818.5
Temperature	K	303.15	303.15	303.2	623.15	308.15	308.2
Pressure	atm	1	2	2	34.02	12	2.4
Mass density	g/cm^3	1.1	0	0.79	0.01	0.01	0

		Liquid by-products	Valeric acid (by-products)	Waste streams		Product
Stream		114	131	107	133	128
Component mass flow						
Levulinic acid	kg/h	0	0	0	0	0
Hydrogen	kg/h	0.01	0	0	0	0
Water	kg/h	11.98	0	4651.1	0	0

Table B2 (*Continued*)

		Liquid by-products	Valeric acid (by-products)	Waste streams		Product
CO_2	kg/h	32.66	0	0.8	0	0
Dibutyl ketone	kg/h	26.26	83.97	0	0	8047.6
3-Hexanone	kg/h	1122.35	0.33	0	0	0
2-Heptanone	kg/h	399.87	14.13	0	0	0
Nonane	kg/h	475.02	12.45	0	0.3	0
Butane	kg/h	161.14	0	0	0	0
Valeric acid	kg/h	55.69	787.63	0.04	0	36.34
Methanol	kg/h	0	19.77	0	39.2	0
Mole flow	kmol/h	23.32	9.14	258.19	1.22	56.93
Mass flow	kg/h	2284.97	918.27	4651.9	39.5	8083.9
Volume flow	L/min	50	16.62	78.77	1.01	165.4
Temperature	K	308.15	303.15	308.15	405	303.15
Pressure	atm	2.4	10	34.02	9	1
Mass density	g/cm^3	0.76	0.92	0.98	0.65	0.81

Table B3
Cost of chemicals.

Chemical	Price	Year of quote
Levulinic acid	$3.21/kg	2009
Hydrogen	$0.116/kg	2008
Methanol	$0.55/kg	2008
Dibutyl ketone	$9.07/kg	2009
Gaseous by-product credit	$0.05/kg (assumed)	2007
Liquid by-product credit	$0.5/kg (assumed)	2007
Pentanoic acid (valeric acid)	$1/kg (assumed)	2007

Table C1
Equipment list and Installed cost for model ‘A’.

Equipment number	Number required	Equipment name	Installed cost in 2007$
P101	1	Feed Pump	$158,651
M101	1	Feed Recycle Mixer	$22,812
H101	1	Reactor Feed Heater	$96,925
R101	2	Reactor	$9,576,990
P102	1	Hydrogen Feed Compressor	$50,276
H102	1	Product Cooler	$400,890
F101	1	Water Flash Separator	$148,155
P103	1	Pressure release valve	$67,137
F102	1	Gas flash separator	$58,210
C101	1	Product Separation Column	$1,834,879
RBC101	1	Column Reboiler	$88,100
CDC101	1	Column condenser	$92,566
H103	1	Product Cooler	$83,695
M102	1	Recycled water purge	$22,811
H104	1	Recycled water heater	$74,900
		Total cost	$12,776,998

Table C2
Equipment list and installed cost for model ‘B’.

Equipment number	Number required	Equipment name	Installed cost in 2007$
P101	1	Feed Pump	$59,321
M101	1	Feed Recycle Mixer	$28,231
R101	2	Reactor	$9,115,373
P102	1	Hydrogen Feed Compressor	$50,903
H101	1	Product Cooler	$1,577,911
F101	1	Water Flash Separator	$135,147
P104	1	Pressure release valve	$63,904
F102	1	Gas flash separator	$58,133
C101	1	Hydrocarbon separation column	$1,759,018
RBC101	1	Column Reboiler	$35,392
CDC101	1	Column condenser	$56,038
M102	1	Recycled water purge	$21,778
H104	1	Recycled water heater	$29,492
M103	1	Methanol mixer	$14,529
C102	1	Nonanone purification column	$997,191
RBC102	1	Column Reboiler	$35,513
CDC102	1	Column condenser	$58,801
P103	1	Column feed pump	$22,050
C103	1	Nonanone purification column	$728,565

Table C2 (*Continued*)

RBC103	1	Column Reboiler	$32,547
CDC103	1	Column condenser	$32,212
C104	1	Nonanone purification column	$748,844
RBC104	1	Column Reboiler	$33,647
CDC104	1	Column condenser	$36,610
C105	1	Methanol recovery column	$350,086
RBC105	1	Column Reboiler	$30,435
CDC105	1	Column condenser	$34,011
H103	1	Pentanoic acid cooler	$26,087
M105	1	Methanol purge	$4,849
M104	1	Product Mixer	$12,932
H102	1	Product Cooler	$32,536
		Total installed cost	$ 16,222,090

Table D1

Summary of process engineering analysis for model ‘A’ (90% pure DBK).

Dibutyl ketone production process engineering analysis			
Production of 90% pure DBK			
Conversion of levulinic acid to DBK			
All values in 2007$			
Minimum DBK selling price	$7.70/kg (90% purity) $6.35/l		
DBK production (mega liters/year)	91.60		
DBK production (metric ton/year)	75453.5		
DBK Yield (liter/metric ton feedstock)	544.2		
Feedstock cost ($/metric ton)	$3210		
Internal rate of return (after-tax)	10%		
Equity percent of total investment	100%		
Reactor	$9,577,058	Feedstock	589.8
Separation system	$2,400,000	Other raw materials	2.2
Other	$800,000	Waste disposal	0.01
Total installed equipment cost	$12,777,058	Utilities	11.0
		Fixed costs	4.1
Added costs	$9,222,942	By-product credits	−13.8
(% of TPI)	42%	Capital depreciation	1.2
		Average income tax[b]	4.3
Total project investment	$22,000,000		
Installed equipment cost/annual liter capacity	$0.14	**Operating costs ($/year)**	
Total project investment/annual liter capacity	$0.24	Feedstock	$539,300,000
		Other raw materials	$2,000,000
Loan rate	N/A	Waste disposal	$9,047
Term (years)	N/A	Utilities	$10,000,000
		Fixed costs	$3,700,000
		By-product credits	−$12,600,000
APV of catalyst cost (million $)	198	Capital depreciation	$1,100,000
Byproduct gases (T/year)	60581.8	Average income tax[b]	$4,000,000
Approx sale price ($/kg)	$0.05		
Revenue (million $/year)	$3.03		
		Specific operating conditions	
Maximum yields (100% of experimental)		Levulinic acid feed (T/day)	480
DBK production (mega liter/year)[a]	92.7	Approx biomass input (metric ton/day)	2000
Experimental yield (liter/metric ton)[a]	551.8	WHSV (kg LA per hour/kg catalyst)	1.0
Current yield (actual/experimental)	98.6%	Catalyst requirement (T)	40.0

[a] Based on final product which includes impurity.

[b] Average income tax is based on NPV of income tax over plant life and NPV of DBK sales over plant life.

Table D2

Summary of process engineering analysis for model ‘B’ (>99% pure DBK).

Dibutyl ketone production process engineering analysis	
Production of 99.5% pure DBK	
Conversion of levulinic acid to DBK	
All values in 2007$	
Minimum dibutyl ketone selling price	$8.49/kg (99.5% purity) $6.92/l
Dibutyl ketone production (mega liter/year)	83.64
Dibutyl ketone production (metric ton/year)	68035.9
Dibutyl ketone yield (liter/metric ton feedstock)	496.9
Feedstock cost ($/metric ton)	$3210
Internal rate of return (after-tax)	10%
Equity percent of total investment	100%

Table D2 (*Continued*)

Reactor	$9,100,000	Feedstock	645.8
Separation system	$2,100,000	Other raw materials	2.7
Purification system	$3,198,911	Waste disposal	0.01
Other	$1,823,180	Utilities	12.6
Total installed equipment cost	$16,200,000	Fixed costs	7.2
		By-product credits	−24.3
Added costs	$11,400,000	Capital depreciation	1.7
(% of TPI)	41%	Average income tax[a]	5.0
Total project investment	$27,600,000		
		Operating costs ($/year)	
Installed equipment cost/annual liter capacity	$0.19	Feedstock	$539,300,000
Total project investment/annual liter capacity	$0.33	Other raw material costs	$2,300,000
		Waste disposal	$4,308
Loan rate	N/A	Utilities	$10,500,000
Term (years)	N/A	Fixed costs	$6,000,000
		By-product credits	−$20,300,000
		Capital depreciation	$1,400,000
APV of catalyst cost (million $)	198.0	Average income tax[a]	$4,200,000
By-product gases (metric ton/year)	60,583		
Approx sale price ($/kg)	$0.05		
Revenue (million $/year)	$3.03	**Specific operating conditions**	
Maximum yields (100% of experimental)		Levulinic acid feed (metric ton/day)	480.0
DBK production (mega liter/year)	85.2	Approx. biomass input (metric ton/day)	2000.0
Experimental yield (liter/metric ton)	506.1	WHSV (kg LA per h/kg catalyst)	1.0
Current yield (actual/experimental)	98%	Catalyst requirement (metric ton)	40.0

[a] Average income tax is based on NPV of income tax over plant life and NPV of DBK sales over plant life.

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