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Simulation and Techno-Economic Evaluation of Large Scale 2.5-Dimethylfuran Production From Fructose

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Conceptual process synthesis (CPS) is an important issue in chemical processing industries. This paper is based on a schematic diagram of 2.5 dimethylfuran (DMF) production from fructose [Y. R. Leshkov, C. J. Barrett, Z. L. Liu, J. A. Dumesic. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. Nature (2007), doi:10.1038/nature05923]. It assessed the general steps of the life cycle of an 2.5-dimethylfuran (DMF) industrial production project. Chemical route synthesis, process development (thermodynamic modeling) and process engineering (defining basic equipment for economic evaluation) were investigated. The process flow diagram (PFD) was made in the commercial process simulator UNISim^{TM}. A literature review on the process was carried out in order to determine which thermodynamic model would be suitable to represent the phase equilibrium. In the system studied (fructose, 1-butanol, sodium chloride, water, chloride acid, hydroxymethylfurfural, 2,5 dimethylfuran) the presence of the sodium chloride affects the phase equilibrium. In this work, consider the salt as simple molecule, rather than distributed charged ions in the solution. This allows the use of the UNIQUAC model. The binary interaction parameters of the model were estimated from experimental data in literature of liquid-liquid equilibrium. The process for DMF production was simulated with these parameters. The process separates water from the 1-butanol and water, 1-butanol and DMF. The material and energy balances were performed by UNISim^{TM} software. Economic evaluation showed that a suitable operational condition could work with 174 mil t/y of fructose and could produce 155 mil t/y of DMF. The cost of DMF was 1.95 U$$/kg. The DMF value and the thermal energy consumption are key issues for a profitable operation of the plant. This analysis suggests that DMF production from fructose deserves serious consideration by investors.

1. Introduction

In an era of increasing oil prices and climate concerns, biofuels have gained more and more attention as potential fuel alternative energy sources. Governments have become active in the target of securing a supply of raw materials and limiting climate change, and many innovative proposals have been made, development work has started and potential candidate fuels have been studied in the energy area (Schaub and Vetter, 2008).

Leshkov et al. (2007) show a catalytic strategy for the production of 2.5 dimethylfuran (DMF) from fructose (a carbohydrate obtained directly from biomass or by the isomerization of glucose) for use as a liquid transportation fuel. Compared to ethanol, 2.5-dimethylfuran has a higher energy density (by 40 %), a higher boiling point (by 20 K), and is not soluble in water. This catalytic strategy creates a route for transforming abundant renewable biomass resources into a liquid fuel suitable or the transportation sector and it is also a CO_2 free process.

The first step in DMF production is to convert fructose to hydroxymethylfurfural (HMF) using an acid catalyst (HCl) and a solvent with a low boiling point in a biphasic reactor. The reactive aqueous phase in the biphasic reactor contains acid and sugar, and the extractive phase contains a partially miscible organic solvent (eg, 1-butanol) that continuously extracts HMF. The addition of a salt to the aqueous phase improves the partitioning of HMF into the extracting phase, and leads to increased HMF yields without the use of high boiling point solvents. Following, water, HCl and solvent evaporate, leading to the precipitation

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of NaCl. Then, HMF is converted into DMF under a copper-ruthenium based catalyst. The final step involves the separation of DMF from the solvent and the non-reacted intermediates. As described below, the process also involves two separation steps. A schematic diagram of fructose conversion to DMF was reported by Leshkov et al. (2007).

The purpose of this paper was to evaluate economically the process for DMF production from fructose. In the present work the following analysis were carried out: Firstly, thermodynamic process modeling was investigated. Following this, the Process Flow Diagram (PFD) was developed from schematic diagram reported by Leshkov et al. (2007). The simulation stage made use data from Leshkov et al. (2007). The thermal energy required for each piece of equipment was assessed with material and energy balances for each system using the UNISim^{TM} software. Each piece of equipment was then approximately sized for economic analysis.

2. Thermodynamic modeling

The work of Debye and Huckel (1923) was the first important academic contribution and established a model for long-range interactions between ions based on the concept of ionic strength. A different family of models was developed using another extension of the Debye-Huckel model to represent the different contributions to Gibbs free energy excess. Implementation of the local composition to electrolytes means it is governed by local interactions such as short-range solvent/solvent, short-range ion/solvent and long-range ion/ion interactions that exist around the immediate neighborhood of a central ionic species (Aznar, 1996). For the contribution of short-range the following models of local composition can be used: Non-Random Two Liquid model (NRTL) (Renon and Prausnitz, 1968), UNIQUAC (Abrams and Prausnitz, (1975) or UNIversal Functional Activity Coefficient (UNIFAC) (Fredenslund et al., 1977). The Debye-Huckel term or one of its variations, such as Fowler and Guggenheim (1949) or the Pitzer (1973) are used for long-range interactions. A series of different combinations have been proposed with these elements.

The hypothesis in this work was that salt should be treated as simple molecule, non-dissociated, rather than as charged ions distributed in the solution. Most works concerning the phase equilibrium in systems containing electrolytes distinguish long-range contributions due to electrostatic forces between ions and between ion and solvent from short-range contributions due to interactions between molecules. Considering the salt as a simple molecule eliminates both contributions and requires only one appropriate model to describe the interactions between all molecules in solution, solvent or electrolyte (Aznar, 1996). Therefore, no specific model for electrolytes was used in this study. The UNIQUAC model was used to obtain the activity coefficient. According to Mock et al. (1986), although the contribution of long-range interaction of the equation of Pitzer-Debye-Huckel is important to obtain the ionic activity coefficient in the aqueous phase, it has little effect on the behavior of the equilibrium phase of the water-organic solvent system. Thus, the effect of the electrolyte was considered only for non-ideality, represented by the adjustable model parameters. The binary interaction parameters of UNIQUAC model were estimated from experimental data (Santis et al., 1976a; Santis et al., 1976b; Catté et al., 1994). A Fortran programming language was used to determine the parameters from experimental data. For the components without experimental data, the UNISIM^{TM} software was used to estimate the remaining binary interaction parameters for the UNIFAC method.

3. Simulation

Simulation of DMF plant production was based on the standard conditions by Leshkov et al. (2007). Figure 1 shows the Process Flow Diagram (PFD) developed from Leshkov et al. (2007). The following unit operations compose the production plant: pumps (P-101, P-102, P-103, P-104, P-105), heat exchangers (E-100, E-101, E-102, E-103, E-104, E-105, E-106, E-108), one reactor for conversion of fructose into HMF (CRV-102) and one reactor for conversion of HMF into DMF (CRV-101), two stripping columns (T-100 and T-101), one distillation column (T-102). The volume of feed was of 30 % fructose and the ratio between the organic phase and the aqueous phase volume was of 3.1 in the biphasic reactor (CRV-102). The conversion of fructose was 75 % and the conversion of HMF to DMF was 100 %. The reactor (CRV-102) works at 453 K and 1350 kPa and the reactor (CRV-101) works at 492 K and 1650 kPa. Unreacted fructose was recycled back into the biphasic reactor (CRV-102). 1-Butanol was then separated from the water in the organic biphasic reactor. Cezário et al. (2009) proposed a separation system for water and 1-butanol composed by two stripping columns, one cooler and one settling tank. The formation of heterogeneous azeotrope makes this separation process more difficult and two liquid phases are formed in the decanter. This system can separate 98 % of 1-butanol. Literature provides various processes for separating 1-butanol from water but the most traditional recovery process is distillation. Other techniques are adsorption, liquid-liquid extraction, evaporation and reverse osmosis. The energy required to recover

1-butanol by adsorption was of 1948 kcal/kg, while the stripping column method required 5789 kcal/kg. Other techniques, such as per evaporation, require 3295 kcal/kg (Qureshi et al., 2005). The last step was separating DMF from 1-butanol. The proposed separation system was composed by a distillation column (T-102) which separated 92 % of DMF. The T-102 operates with reflux rate of 85 kgmol/h and top component (DMF) fraction of 0.9. The 1-butanol recovered in the T-102 was recycled.
Thus, material and energy balances were then solved using UNISim^{TM} software. The Tables 1 and 2 show the energy spending for pumps and Heat Exchangers.

Table 1: Energy spending for pumps

Pump	Heaty Duty (kJ/s)
P-101	2.581
P-102	0.427
P-103	0.402
P-104	0.294
P-105	0.233
P-100	3.426

Table 2: Energy spending for Heat Exchangers

Heat Exchanger	Heaty Duty (kJ/s)	Mass flow (kg/s)
E-102	3.025×10^2	1.15
E-103	159.88	0.25
E-104	134.30	0.28
E-105	107.53	0.24
E-108	51.06	0.14
E-101	466.67	1.22
E-106	961.11	2.05
E-100	21722.22	21.89

4. Economic evaluation

The economic evaluation was based on the spreadsheets by Peters & Timmerhaus (2003). The following steps were used by performed the economic analysis.
i) On the sheet '**Capital Inv**.' The estimated current total purchased cost of the equipment was entered;
ii) On the sheet '**Materials & Labor**' the product and the raw materials prices, flow rates, and the labor requirements were entered;
iii) On the sheet '**Utilities**' the quantity of each utility needed annually was entered in appropriate units. The total annual utilities cost was transferred to sheet '**Annual TPC**';
iv) The '**Depreciation**' sheet was used only if the user wished to change the default (5-year **Modified Accelerated Cost Recovery System (**MACRS) depreciation method);
v) On the '**Annual TPC**' sheet, all values were calculated from information available on other sheets. The Calculated annual TPC was transferred to '**Evaluation**';
vi) The sheet '**Evaluation**' used values from other sheets to calculate the common profitability measures. All calculations in 'Evaluation' are made in current (i.e. inflated) dollars.
Each piece of equipment was roughly sized from material and energy balance and the approximate cost determined. Costs of equipment operating at ambient pressure and using carbon steel, were estimated by Eq. (1) (Turton et al., 2003).

$$\log Cp^o = K_1 + K_2 \log(A) + K_3 (\log(A))^2 \tag{1}$$

where A is the equipment capacity or size parameter and K_1, K_2 and K_3 are the parameters (Turton et al., 2003). The effect of time, operating conditions and material construction on purchased equipment cost was corrected by time factor (I), material factor (F_M) and conditions factor (F_P). Purchased equipment cost is then expressed by Eq (2):

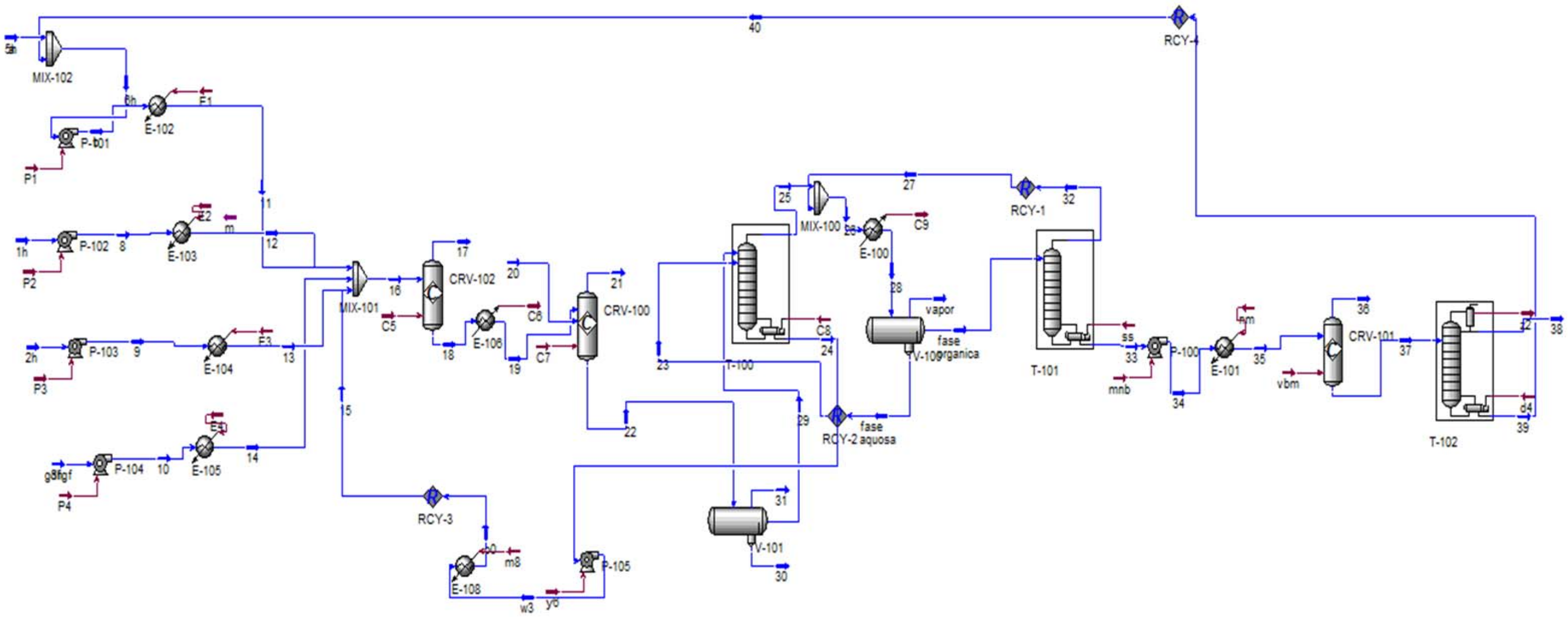

Figure 1: Process Flow Diagram (PFD) for DMF production from fructose

$$Cp = Cp^0 \times F_M \times F_P \times I \quad (2)$$

In this work, inflation was accounted for by the Chemical Engineering Plant Cost Index (Lozowski, 2013). In Table 3 it is observed that the higher costs to produce DMF are fructose and solvent (1-butanol).

Table 3: *Price and annual amount of raw materials and product*

Material	**material**	**Price (US$$/kg)**	**Annual amount (10^6 kg/y)**	**Annual value (10^6 US$$/y)**
DMF	Product	variable	2.217	0.88
Fructose	Raw material	0.78 (variable)	2.484	1.94(62 %)
NaOH	Raw material	0.015	0.05	0.0007(0.02 %)
HCl	Raw material	0.295	0.745	0.22(7.7 %)
1-butanol	Raw material	1.72	0.431	0.7906(23 %)
water	Raw material	0.08	16.312	1.30(2.6 %)
NaOH	Raw material	0.10	25	2.5(2.7 %)
Hydrogen	Raw material	10	0.13834	1.3834(1.4 %)

Chemical and utility costs were obtained and a discounted cash flow analysis was performed to determine profitability. The quantities of chemical material, utilities and production of DMF were doubled, tripled, etc, from the simulated plant, to achieve sale price and cost DMF similar to gasoline and ethanol. However, the equipment cost increased according to Eq. (3).

$$\text{Equipament cost} = N^{0.6} \quad (3)$$

where N is the scale factor with values of N = 2, 5, 10, etc.

Thus, the estimated cost of the equipment was US$ $12 \cdot 10^6$, fixed capital investment was US$ $58 \cdot 10^6$, direct cost were US$ $41 \cdot 10^6$, indirect costs were US$ $17 \cdot 10^6$, working capital was US$ $10 \cdot 10^6$ and total capital investment was US$ $68 \cdot 10^6$. From economic evaluation the value and cost DMF was 2.68 US$/kg and 1.95 US$/kg, respectively. For this analysis, the plant is economically feasible for a scale factor of thirty (N= 30).

In Table 4 it is observed that the sale price of DMF can be compared with the gasoline. The cost of DMF decreases with the increase of the conversion of fructose to HMF and with the decrease in fructose price.

Table 4: Sale price/cost (US$/kg) of DMF for several values of conversions in reactor CRV-102 and of fructose prices (scale factor 30)

	Conversion (75 %)	Conversion (80 %)	Conversion (85 %)
Fructose price, 0.78 US$/kg	2.68/1.95	2.60/1.89	2.55/1.85
Fructose price, 0.50 US$/kg	2.27/1.60	2.20/1.56	2.15/1.52
Fructose price, 0.10 US$/kg	1.68/1.10	1.63/1.07	1.60/1.05

5. Conclusions

The following conclusions can be drawn from the facts presented in the above review. Considering 174 fructose t/y consumption and a U$$ 2.68/kg DMF selling price, the obtained results were: DMF annual production of 155 mil t, total capital invested of U$$ 58 million; equipment invested of U$$ 12 million; payback time of 0.4 y; return on investment of 222 %. For this analysis, the plant is economically feasible, from comparison with a reference market of 15.0 %/y (return on investment) with a 3.6 y payback period. This analysis suggests that DMF production from fructose deserves serious consideration by investors.

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