Techno-Economic Evaluation of Large Scale 2.5-Dimethylfuran Production from Fructose

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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 & Vetter, 2008).

A number of factors must be considered when evaluating biofuels: technical factors (raw materials, supply, conversion and engines), economic (engine modification cost, infrastructure) and ecological/political (greenhouse gases, land use efficiency, oil dependence reduction) (Festel, 2008).

An end-user survey assessed car customer acceptance and attitude toward biofuels and revealed that their main demands are: price (48%), biofuel price should not exceed fossil fuels prices and there should be no cost in engine modification; environment (24%); consumption (19%) and performance (9%) (Festel, 2008).

Since customers consider the final cost as a decisive factor, the economic analysis is an important tool in the assessment of the success of biofuel production process and consequent market success. Achieving economic viability used to be the key to success, but today, other factors are important, such as sustainability.

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 percent), a higher boiling point (by 20K), and is not soluble in water. This catalytic strategy creates a route for transforming abundant renewable biomass resources into a liquid fuel suitable for the transportation sector and it is also a CO₂ free process.

The first step in 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 precipitation 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 is to evaluate economically the process production of DMF 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 makes 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™ software. Each piece of equipment is then approximately sized for economic analysis.

2. Thermodynamic modeling

The thermodynamic equilibrium of a system consisted of a multicomponent mixture takes place when temperature, pressure and chemical potential of components are equated between the phases, for each component. Although there are other basic criteria for system equilibrium, the minimization of Gibbs free energy is the condition which ensures equilibrium. Salt can affect the solubility of the system components with the formation of complex associations. In general it can be inferred that the particles (molecules, ions, or both) of dissolved salt tend to attract molecules from one of the system components more strongly than others.

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), UNIUQUAC (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. Two different models are then used for each contribution type. Considering 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 is 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, 1976b), from Catté et al. (1994) and for the UNIFAC method. The tables 2, 3 e 4 show the data experimental used to estimate the binary interactions parameters. A Fortran programming language was used to determine the parameters from experimental data. The UNISIM™ software was used to estimate parameters for the UNIFAC method.

| Water   | 1-butanol | DMF   | Fructose | HCl   | HMF   | NaCl  |
|---------|-----------|-------|----------|-------|-------|-------|
| Water   | -         | 89.22*| 1543'    | -153.35**| 1160' | 1361' | -455* |
| 1-butanol| 208*      | -     | 383'     | 223'  | 1421' | 530'  | 863*  |
| DMF     | 249'      | -90'  | -        | 73'   | -     | -146' | -371' |
| Fructose| 324**     | 91'   | 892'     | -     | -197' | 1.412'| 160'  |
| HCl     | -674'     | -179' | -        | 399'  | -     | 702'  | -266' |
| HMF     | -121'     | -1155'| 564'     | 162'  | 2,776'| -     | 2479' |
| NaCl    | -165*     | 1251* | 1793'    | 354'  | 2943' | 1391' |-       |

* Binary interaction parameters of UNIQUAC model estimated from experimental data from Santis et al. (1976a, 1976b).
** Catté et al. (1994).
' Binary interaction parameter estimated from UNIFAC method.

Table 1. Binary interaction parameters of UNIQUAC model

| Aqueous Phase | NaCl  | Water | 1-butanol | NaCl  | Water | 1-butanol | NaCl  |
|---------------|-------|-------|-----------|-------|-------|-----------|-------|
| 92.60         | 7.4   | -     | 20.4      | 79.6  | -     | 0.005     |
| 92.04         | 6.8   | 1.16  | 18.78     | 81.2  | 0.025 |
| 91.64         | 6.1   | 2.26  | 17.45     | 82.5  | 0.045 |
| 90.85         | 5.8   | 3.35  | 16.64     | 83.3  | 0.061 |
| 90.60         | 5.0   | 4.40  | 15.43     | 84.5  | 0.074 |
| 89.96         | 4.6   | 5.44  | 14.6      | 85.3  | 0.086 |
| 89.16         | 4.4   | 6.44  | 14.1      | 85.8  | 0.095 |
| 87.84         | 3.7   | 8.46  | 13.29     | 86.6  | 0.110 |
| 86.30         | 3.3   | 10.4  | 12.48     | 87.4  | 0.122 |
| 85.10         | 2.7   | 12.2  | 11.37     | 88.5  | 0.130 |
| 83.50         | 2.5   | 14.0  | 10.66     | 89.2  | 0.138 |
| 82.20         | 2.0   | 15.8  | 8.75      | 90.1  | 0.144 |
| 80.90         | 1.7   | 17.4  | 9.05      | 90.8  | 0.148 |
| 79.40         | 1.5   | 19.1  | 8.55      | 91.3  | 0.153 |
| 78.00         | 1.3   | 20.7  | 7.94      | 91.9  | 0.156 |
| 76.70         | 1.1   | 22.2  | 7.34      | 92.5  | 0.159 |
| 75.20         | 0.9   | 23.9  | 7.04      | 92.8  | 0.162 |
| 74.00         | 0.8   | 25.2  | 6.54      | 93.3  | 0.164 |
| 73.30         | 0.8   | 25.9  | 6.43      | 93.4  | 0.167 |
| 73.30         | 0.8   | 25.9  | 6.23      | 93.6  | 0.167 |

Table 2. Liquid-liquid equilibrium in the system water-1-butanol-NaCl (Santis et al., 1976a)
| Aqueous Phase | Organic Phase |
|--------------|---------------|
| water | 1-butanol | NaCl | water | 1-butanol | NaCl |
| 92.90 | 7.10 | - | 20.60 | 79.4 | - |
| 92.43 | 6.42 | 1.15 | 18.77 | 81.2 | 0.026 |
| 92.04 | 5.70 | 2.26 | 17.75 | 82.2 | 0.045 |
| 91.22 | 5.44 | 3.34 | 16.74 | 83.2 | 0.061 |
| 90.59 | 5.00 | 4.41 | 15.92 | 84.0 | 0.075 |
| 89.96 | 4.59 | 5.45 | 15.31 | 84.6 | 0.086 |
| 89.28 | 4.24 | 6.48 | 14.70 | 85.2 | 0.096 |
| 87.9 | 3.60 | 8.50 | 13.69 | 86.2 | 0.111 |
| 86.46 | 3.04 | 10.5 | 12.68 | 87.2 | 0.123 |
| 85.01 | 2.59 | 12.4 | 11.87 | 88.0 | 0.132 |
| 83.35 | 2.45 | 14.2 | 11.26 | 88.6 | 0.140 |
| 82.19 | 1.81 | 16.0 | 1.15 | 89.7 | 0.146 |
| 80.79 | 1.51 | 17.7 | 9.35 | 90.5 | 0.150 |
| 79.67 | 1.23 | 19.1 | 8.74 | 91.1 | 0.155 |
| 77.97 | 1.03 | 21.0 | 7.84 | 92.0 | 0.158 |
| 76.51 | 0.89 | 22.6 | 7.44 | 92.4 | 0.161 |
| 75.15 | 0.75 | 24.1 | 6.94 | 92.9 | 0.164 |
| 73.81 | 0.69 | 25.5 | 6.63 | 93.2 | 0.166 |
| 73.34 | 0.68 | 26.0 | 6.43 | 93.4 | 0.169 |

Table 3. Liquid-liquid equilibrium in the system water-1-butanol-NaCl (Santis et al., 1976a)

| Aqueous Phase | Organic Phase |
|--------------|---------------|
| water | 1-butanol | NaCl | water | 1-butanol | NaCl |
| 93.40 | 6.60 | - | 21.40 | 78.6 | - |
| 92.85 | 5.96 | 1.19 | 19.68 | 80.3 | 0.021 |
| 92.44 | 5.25 | 2.31 | 18.36 | 81.6 | 0.041 |
| 91.88 | 4.70 | 3.42 | 17.54 | 82.4 | 0.060 |
| 90.86 | 4.61 | 4.53 | 16.83 | 83.1 | 0.072 |
| 90.21 | 4.21 | 5.58 | 16.31 | 83.6 | 0.085 |
| 89.49 | 3.86 | 6.65 | 15.50 | 84.4 | 0.095 |
| 88.04 | 3.27 | 8.69 | 14.49 | 85.4 | 0.111 |
| 86.62 | 2.78 | 10.6 | 13.58 | 86.3 | 0.122 |
| 85.19 | 2.31 | 12.5 | 12.77 | 87.1 | 0.131 |
| 83.70 | 1.90 | 14.4 | 11.96 | 87.9 | 0.139 |
| 82.10 | 1.70 | 16.2 | 11.25 | 88.6 | 0.146 |
| 80.92 | 1.28 | 17.8 | 10.35 | 89.5 | 0.151 |
| 79.59 | 1.01 | 19.4 | 9.44 | 90.4 | 0.156 |
| 78.18 | 0.82 | 21.0 | 8.84 | 91.0 | 0.160 |
| 76.74 | 0.66 | 22.6 | 8.34 | 91.5 | 0.163 |
| 75.36 | 0.54 | 24.1 | 7.83 | 92.0 | 0.166 |
| 73.9 | 0.50 | 25.6 | 7.53 | 92.3 | 0.170 |
| 73.42 | 0.48 | 26.1 | 7.03 | 92.8 | 0.173 |
| 73.42 | 0.48 | 26.1 | 7.03 | 92.8 | 0.173 |

Table 4. Liquid-liquid equilibrium in the system water-1-butanol-NaCl (Santis et al., 1976b)
3. Simulation

Simulation of DMF plant production was based on the standard conditions by Leshkov et al. (2007) from which it was developed a process flow diagram (PFD). The following unit operations compose the production plant: pumps, heat exchangers, 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 is 75% and the conversion of HMF to DMF is 100%.

Unreacted fructose was recycled back into the biphasic reactor. 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 turns 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 is of 1948 kcal/kg while the stripping column method requires 5789 kcal/kg. Other techniques such as perevaporation requires 3295 kcal/kg 1-butanol (Qureshi et al., 2005). The last step was to separate 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 kglmol/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™ software and is showed in Table 5.

|        | 1h  | 2h  | 3h  | 5h  | 8    |
|--------|-----|-----|-----|-----|------|
| Temperature (°C) | 25  | 25  | 25  | 25  | 25   |
| Pressure (kPa)    | 101 | 101 | 101 | 101 | 1351 |
| Massic flow (kg/h)| 896 | 1000| 864 | 52  | 896  |
| Enthalpy (kJ/kgmol) | -275200 | -290600 | -290500 | -326600 | -275200 |
| Composition (massic fraction) | | | | | |
| water             | 0.9 | 0.7 | 0.5372 | -   | 0.9  |
| 1-butanol         | -   | -   | -     | 1   | -    |
| Fructose          | -   | -   | -     | -   | -    |
| Hmf               | -   | -   | -     | -   | -    |
| NaCl              | -   | -   | 0.4628| -   | -    |
| HCl               | 0.1 | -   | -     | -   | 0.1  |
| NaOH              | -   | -   | -     | -   | -    |
| DMF               | -   | -   | -     | -   | -    |
| 9                 |     | 10  | 11   | 12  | 13   |
| Temperature (°C) | 25  | 25  | 180  | 180 | 180  |

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| Temperature (°C) | 180 | 180 | 180 | 180 | 37 |
|-----------------|-----|-----|-----|-----|----|
| Pressure (kPa)  | 1351| 1351| 1351| 1351| 1351|
| Massic flow (kg/h) | 1000| 864 | 4142| 896 | 1000|
| Enthalpy (kJ/kmol) | -290600| -290500| -326600| -263000| -278700|

### Composition (massic fraction)

| Água | 0.7 | 0.5372 | - | 0.9 | 0.9589 |
| 1-butanol | - | - | 1 | - | - |
| Frutose | 0.3 | - | - | - | 0.0411 |
| Hmf | - | - | - | - | - |
| NaCl | - | 0.4628 | - | - | - |
| HCl | - | - | - | 0.1 | - |
| NaOH | - | - | - | - | - |
| DMF | - | - | - | - | - |

| 14 | 16 | 15 | 18 | 19 |
|-----|-----|-----|-----|-----|
| Temperature (°C) | 180 | 180 | 180 | 180 | 37 |
| Pressure (kPa) | 1351 | 1351 | 1351 | 1351 | 1351 |
| Massic flow (kg/h) | 864 | 7392 | 489 | 7392 | 7392 |
| Enthalpy (kJ/kmol) | -260600 | -291400 | -274800 | -277200 | -294200 |

### Composition (massic fraction)

| Water | 0.7901 | 0.3250 | 0.8825 | 0.3250 | 0.3250 |
| 1-butanol | - | 0.5603 | - | 0.5603 | 0.5603 |
| Fructose | - | 0.0484 | 0.1174 | 0.0121 | 0.0121 |
| Hmf | - | - | - | 0.0363 | 0.0363 |
| NaCl | 0.2098 | 0.0541 | - | 0.0541 | 0.0541 |
| HCl | - | 0.0122 | - | 0.0218 | 0.0218 |
| NaOH | - | - | - | 0 | 0 |
| DMF | - | 0.00005 | - | 0 | 0 |

| 22 | 29 | 30 | 25 | 24 |
|-----|-----|-----|-----|-----|
| Temperature (°C) | 37 | 37 | 37 | 80 | 81 |
| Pressure (kPa) | 1351 | 1351 | 1351 | 50 | 50 |
| Massic flow (kg/h) | 7592 | 4876 | 2716 | 23575 | 489 |
| Enthalpy (kJ/kmol) | -296500 | -311400 | -240600 | -282400 | -282400 |

### Composition (massic fraction)

| Water | 0.3353 | 0.0887 | 0.7781 | 0.7995 | 0.8822 |
| 1-butanol | 0.5456 | 0.8444 | 0.0091 | 0.1876 | - |
| Fructose | 0.0118 | 0.0118 | 0.01168 | - | 0.1178 |
| Hmf | 0.0353 | 0.0549 | - | 0.01138 | - |
| NaCl | 0.0719 | - | 0.2011 | - | - |
| HCl | - | - | - | - | - |
| NaOH | - | - | - | - | - |
| DMF | - | - | - | 0.0015 | - |

| 26 | 27 | Organic phase | Aqueous phase | 32 |
| Temperature (°C) | 74 | 71 | 36 | 36 | 71 |
|-----------------|----|----|----|----|----|
| Pressure (kPa)  | 50 | 50 | 50 | 50 | 50 |
| Massic flow (kg/h) | 78804 | 55229 | 59614 | 19189 | 55230 |
| Enthalpy (kJ/kgmol) | -224500 | -197800 | -245800 | -284100 | -197800 |

Composition (massic fraction)

| Water          | 0.2585 | 0.0275 | 0.0255 | 0.4822 | 0.02752 |
|----------------|--------|--------|--------|--------|---------|
| 1-butanol      | 0.1716 | 0.1647 | 0.2217 | 0.01592 | 0.1647 |
| Fructose       | -      | -      | -      | -      | -       |
| Hmf            | 0.00341 | - | 0.004517 | - | - |
| NaCl           | -      | -      | -      | -      | -       |
| HCl            | -      | -      | -      | -      | -       |
| NaOH           | -      | -      | -      | -      | -       |
| DMF            | 0.5665 | 0.8077 | 0.7483 | 0.00177 | 0.8077 |

| Temperature (°C) | 100 | 101 | 219 | 71 | 99 |
|-----------------|-----|----|----|----|----|
| Pressure (kPa)  | 50  | 1650 | 1650 | 50 | 50 |
| Massic flow (kg/h) | 4384 | 4384 | 4384 | 290 | 4094 |
| Enthalpy (kJ/kgmol) | -390900 | -308800 | -279700 | -215100 | -310900 |

Composition (massic fraction)

| Water          | - | - | - | - | - |
|----------------|---|---|---|---|---|
| 1-butanol      | 0.9388 | 0.9388 | 0.9388 | 0.07891 | 0.9999 |
| Fructose       | - | - | - | - | - |
| Hmf            | 0.0611 | 0.0611 | 0.0611 | - | - |
| NaCl           | - | - | - | - | - |
| HCl            | - | - | - | - | - |
| NaOH           | - | - | - | - | - |
| DMF            | - | - | - | 0.9221 | 0.000086 |

Table 5.
Fig. 1. Material and energy balance for each stream in DMF production plant.

4. Economic evaluation

The economic evaluation was based on the spreadsheets by Peters & Timmethaus (2003). The following steps were used to perform the economic analysis.

i. On the sheet ‘Capital Inv.’ The estimated current total purchased cost of the equipment was entered. The results are showed in Table 7.

ii. On the sheet ‘Materials & Labor’ the product prices and flowrates, the raw materials prices and flow rates, and the labor requirements were entered. The results are showed in Table 8.

iii. On the sheet ‘Utilities’ the quantity of each utility needed annually was entered in appropriate units. The total annual utilities cost is transferred to sheet ‘Annual TPC’;

iv. The ‘Depreciation’ sheet is used only if the user wishes 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’. The results are showed in Table 9.

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).

\[ \log C_p^o = K_1 + K_2 \log(A) + K_3 (\log(A))^2 \]  

(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
| Equipment number | equipment  | Parameter equipment          | Equipment cost ($) |
|------------------|------------|-----------------------------|--------------------|
| P-101            | pump       | flow: 4.97 m³/h              | 3814               |
| P-102            | pump       | flow: 0.92 m³/h              | 2910               |
| P-103            | pump       | flow: 0.864 m³/h             | 2898               |
| P-104            | pump       | flow: 0.63 m³/h              | 2845               |
| P-105            | pump       | flow: 0.54 m³/h              | 2823               |
| P-100            | pump       | flow: 5.27 m³/h              | 4670               |
| E-102            | heater     | Heat duty: 302,5 KW          | 64862              |
| E-103            | heater     | Heat duty: 160 KW            | 42107              |
| E-104            | heater     | Heat duty: 134 KW            | 37333              |
| E-105            | heater     | Heat duty: 107 KW            | 320119             |
| E-106            | heater     | Heat duty: 8790 KW           | 637790             |
| E-108            | heater     | Heat duty: 100 KW            | 30610              |
| E-100            | cooler     | Water flow: 198 m³/h         | 11421              |
| E-101            | heater     | Heat duty: 467 KW            | 87085              |
| CRV-102          | reactor    | Heat duty: 10000 KW          | 2917722            |
| CRV-100          | reactor    | Heat duty: 344,75 KW         | 22354              |
| CRV-101          | reactor    | Heat duty: 10000 KW          | 2917722            |
| T-100            | stripping column | Height: 4 m; diameter: 1m | 15003              |
| T-101            | stripping column | Height: 4 m; diameter: 1m | 15003              |
| T-102            | destilation column | Height: 4 m; diameter: 1m | 15003              |
| **Total**        |            |                             | **1609365**        |

Table 6. Equipment parameter

| | Fraction of delivered equipment | Cost directs |
|---|---------------------------------|--------------|
| | Solid processing plant (A) | Solid fluid processing plant (B) | Fluid processing plant (C) | % choseed (B) | Calculated values, million ($) |
| **Cost directs** | | | | | **1.609** |
| Purchased equipment, E' | 0.10 | 0.10 | 0.10 | 0.10 | 0.1604 |
| Delivery, fraction of E' | 0.45 | 0.39 | 0.47 | 0.39 | 0.6903 |
| Instrumentation & controls (installed) | 0.18 | 0.26 | 0.36 | 0.26 | 0.460 |
| Piping (installed) | 0.16 | 0.31 | 0.68 | 0.31 | 0.548 |
| Eletrical systems (installed) | 0.10 | 0.10 | 0.11 | 0.10 | 0.177 |

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## Fraction of delivered equipment

|                              | Solid processing plant (A) | Solid fluid processing plant (B) | Fluid processing plant (C) | % chosen (B) | Calculated values, million ($) |
|------------------------------|----------------------------|---------------------------------|---------------------------|-------------|--------------------------------|
| Buildings (including services) | 0.25                       | 0.29                            | 0.18                      | 0.29        | 0.513                          |
| Yard improvements            | 0.15                       | 0.12                            | 0.10                      | 0.12        | 0.212                          |
| Service facilities (installed) | 0.40                       | 0.55                            | 0.70                      | 0.55        | 0.973                          |
| Total direct costs           |                            |                                 |                           |             | 5.345                          |

### Indirect costs

|                              | Engineering and supervision | Construction expenses | Legal expenses | Contractor’s fee | Contingency | Total indirect costs |
|------------------------------|-----------------------------|-----------------------|----------------|-----------------|-------------|----------------------|
|                              | 0.33                        | 0.32                  | 0.33           | 0.32            | 0.32        | 0.566                |
|                              | 0.39                        | 0.41                  | 0.34           | 0.41            | 0.34        | 0.602                |
|                              | 0.04                        | 0.22                  | 0.04           | 0.22            | 0.04        | 0.071                |
|                              | 0.35                        | 0.44                  | 0.37           | 0.44            | 0.37        | 0.655                |
| Total indirect costs         |                            |                       |                |                 |             | 2.23                 |

|                              | Fixed capital investment    | Working capital | Total capital investment |
|------------------------------|-----------------------------|-----------------|--------------------------|
|                              | 7.575                       | 0.70            | 8.903                    |

Table 7. Estimation of capital investment by percentage of delivered equipment method

| Material   | Material classification | Price (US$/kg) | Annual amount (million kg/year) | Annual value (million US$/year) |
|------------|-------------------------|----------------|---------------------------------|---------------------------------|
| DMF        | Product                 | variable       | 2.217                           | 0.88                            |
| Fructose   | Raw material            | 0.78 (variable)| 2.484                           | 1.94(62%)                       |
| NaCl       | 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%)                       |
| H2         | Raw material            | 10             | 0.13834                         | 1.3834(1.4%)                    |

Table 8. Annual raw material costs and products values
| Item (A)                  | Factor (B) | Basis (C) | Basis Cost (million) US$/year (D) | Cost (million) US$/year (E) |
|--------------------------|------------|-----------|----------------------------------|-----------------------------|
| 1. Raw materials         |            |           |                                  |                             |
| 2. operating labor (M)   |            |           |                                  |                             |
| 3. operating supervision | 0.15       | de (2)    | 0.885                            | 0.133                       |
| 4. utilities             |            |           |                                  |                             |
| 5. maintenance and repairs (MR) | 0.06 | de FCI | 1.407                            | 0.46                       |
| 6. operating supplies    | 0.15       | de (5)    | 0.084                            | 0.07                       |
| 7. laboratory charges    | 0.15       | de (2)    | 0.885                            | 0.133                       |
| 8. Royalties             | 0.01       | de c₀     | 3.090                            | 0.08                       |
| 9. catalysts and solvents | 0         |           |                                  | 2.5                        |

**Variable cost**  
6.536

| Item (A)                  | Factor (B) | Basis (C) | Basis Cost (million) US$/year (D) | Cost (million) US$/year (E) |
|--------------------------|------------|-----------|----------------------------------|-----------------------------|
| 10. taxes (property)     | 0.02       | de FCI    | 1.407                            | 0.156                       |
| 11. financing (interest) | 0          | de FCI    | 1.407                            | 0                           |
| 12. insurance            | 0.01       | de FCI    | 1.407                            | 0.014                       |
| 13. rent                 | 0          |           | 1.407                            | 0.078                       |
| 14. depreciation         |            |           |                                  | Calculated separately      |
| 15. plant overhead, general | 0.6       |           | 1.102                            | 0.891                       |
| 16. administration       |            |           |                                  | 0.661                       |
| 17. manufacturing cost   |            |           |                                  | 7.660                       |
| 18. administration       | 0.2        | de (2), (5) | 1.102                           | 0.297                       |
| 19. distribution & selling | 0.05     | de c₀     | 3.090                            | 0.437                       |
| 20. Research & development | 0.04     | de c₀     | 3.090                            | 0.350                       |

General expense

Total product cost without depreciation = c₀

8.744

Table 9. Annual total product cost at 100 % capacity

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:

\[
C_p = C_p^0 \times F_M \times F_P \times I
\]  

(2)
In this work, inflation was accounted for by the Chemical Engineering Plant Cost Index (Lozowski, 2010). According to Table 8 the price of raw material and solvent are the more expensive.

With chemical and utility cost 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). For all sale price and cost DMF from Tables 5, 6 e 7 the profitability measures were: 15.0%/year (return on investment) and a 3.6 year payback period.

The conversion and the price fructose were changed too. The tables 10, 11 and 12 show the results.

|                         | Conversion (75%) | Conversion (80%) | Conversion (85%) |
|-------------------------|------------------|------------------|------------------|
| Fructose price, 0.78 US$/kg | 6.00/3.94        | 5.90/3.83        | 5.80/3.75        |
| Fructose price, 0.50 US$/kg | 5.70/3.59        | 5.60/3.49        | 5.40/3.42        |
| Fructose price, 0.10 US$/kg | 5.20/3.10        | 5.00/3.00        | 4.90/2.94        |

Table 10. Sale price of DMF/cost (US$/kg) of DMF to several conversions in reactor CRV-102 and various prices of fructose (standard plan used in the simulation).

|                         | Conversion (75%) | Conversion (80%) | Conversion (85%) |
|-------------------------|------------------|------------------|------------------|
| Fructose price, 0.78 US$/kg | 3.70/2.68        | 3.60/2.59        | 3.52/2.54        |
| Fructose price, 0.50 US$/kg | 3.30/2.33        | 3.20/2.26        | 3.13/2.22        |
| Fructose price, 0.10 US$/kg | 2.70/1.83        | 2.63/1.78        | 2.58/1.74        |

Table 11. Sale price of DMF/cost (US$/kg) of DMF to several conversions in reactor CRV-102 and various prices of fructose (scale factor 12).

|                         | 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        |

Table 12. Sale price of DMF/cost (US$/kg) of DMF to several conversions in reactor CRV-102 and various prices of fructose (scale factor 30).

In table 12 observes 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 price decrease of fructose.

\[ \text{Equipment cost} = N^{0.6} \] (3)
Where \( N \) is the scale factor with values of \( N = 2, 5, 10, \) etc.

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

5. Conclusions

The following conclusions can be drawn from the facts presented in the above review. In the thermodynamic analysis salt is considered a solute, so it’s possible to use the model UNIQUAC (Mock et al., 1986). The estimation of binary interaction parameters for UNIQUAC in the system water-butanol-salt was carried out with Fortran software from liquid-liquid equilibrium data and UNIFAC (UNIQUAC Functional-group Activity Coefficient) method was used to estimate remain parameters. The separation system (composed by two stripping columns, one cooler and one settling tank) used to separate 1-butanol and water recovery 98% of 1-butanol. The separation system (composed by distillation column) used to separate DMF recovery 92 % of DMF. Economic evaluation showed that a suitable operational plant could work with 12.4 tons/year of fructose. It could produce 11.1 tons/year of DMF. The fixed capital investment in plant and equipment is estimated at U.S. $ 58 million and U.S. $ 12 million, respectively. The DMF value was 2.69 U.$. $/kg. For this analysis, the plant is economically feasible, from comparison with a reference market of 15.0 %/year (return on investment) with a 3.6 year payback period. This analysis suggests that DMF production from fructose deserves serious consideration by investors.

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Chemical engineering applications have been a source of challenging optimization problems in terms of economics and technology. The goal of this book is to enable the reader to get instant information on fundamentals and advancements in chemical engineering. This book addresses ongoing evolutions of chemical engineering and provides overview to the state of the art advancements. Molecular perspective is increasingly important in the refinement of kinetic and thermodynamic molding. As a result, much of the material was revised on industrial problems and their sophisticated solutions from known scientists around the world. These issues were divided into two sections, fundamental advances and catalysis and reaction engineering. A distinct feature of this text continues to be the emphasis on molecular chemistry, reaction engineering and modeling to achieve rational and robust industrial design. Our perspective is that this background must be made available to undergraduate, graduate and professionals in an integrated manner.

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