Removal of Carboxylic Acids from Fischer-Tropsch Aqueous Product

by

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Abstract

Fischer–Tropsch is a process whereby a gaseous mixture of carbon monoxide (CO) and hydrogen (H_2), called syngas, is converted into hydrocarbons, oxygenates and water. After the Fisher–Tropsch reaction the reaction product is cooled down and one of the product phases is a liquid stream known as the aqueous product, or reaction water. The water also contains around 2 to 6% oxygenates, mainly light alcohols, carbonyls and carboxylic acids. Most of the dissolved alcohols and carbonyls can be recovered by distillation, resulting in a carboxylic acid containing bottom product, called acid water. The acid water contains around ~1 % carboxylic acids of which ~85% is acetic acid, with lower amounts of propionic and butyric acids. Due to the presence of carboxylic acids, the pH is low and the chemical oxygen demand of the water is high. It cannot be directly discharged into water bodies, or used as process water, so it needs to be treated first.

Currently the industry is treating the acid water biologically using aerobic or anaerobic processes, but in all cases the facilities are located in warm climates. The overall objective of the research was to find an alternative technique for treating Fischer–Tropsch acid water that is suitable for application in Canada, which has a cold climate. The alternative techniques for treating the acid water had to be both technically feasible and economically viable.

Three processes were identified as potential alternatives for treating Fischer-Tropsch acid water: (1) Fractional freezing, (2) Electrolysis, and (3) Catalytic decomposition. For each process aqueous product effluent used for experiments was close to industrial acid water. Each process was evaluated experimentally to demonstrate proof of concept and generate engineering data. The experimental work was followed by a conceptual design to demonstrate technical feasibility for meeting Canadian effluent standards, and determine the cost. This was also done for biological treatment processes, which served as base case for an economic evaluation on the same design basis.

It was found that all three of the alternative processes were technically feasible, but that fractional freezing was the most cost competitive with biological treatment.

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Chapter 1: Introduction

1. Background

The Fischer-Tropsch process is named after its two inventors Franz Fischer and Hans Tropsch who developed the process at Kaiser Wilhelm Institute for Coal Research in the Ruhr, Germany. By 1938 there were nine plants in operation in Germany having a combined capacity of about 660×10^3 t per year [1]. After Second World War these plants were shut down and never started up again.

A Fischer-Tropsch plant with a capacity of 360×10^3 t per year was built and operated during 1950s in Brownsville, TX. This plant was based on syngas produced form methane and because of sharp increase in price of methane this plant was shut down later.

At the same time, coal based Fischer-Tropsch plant was built in Sasolburg, South Africa. The vast oil fields of Middle East were discovered in 1950s, which resulted in a low oil price, but this facility remained operational due to cheap local coal and government policy [2].

In 1973 with the 'oil crisis', the price of crude oil increased and interest in synthetic fuels processes were rekindled. During 1980s, Sasol constructed two large coal-based Fischer-Tropsch plants. The capacity of all the three Sasol plants at that point was about 6000×10^3 t per year [1].

The first large scale Fischer-Tropsch plants using methane as feed were built in 1990s, Mossgas plant in South Africa (1000 × 10^3 t per year) and Shell plant at Bintuli, Malaysia (500 × 10^3 t per year) [1].

Today Fischer-Tropsch synthesis is still used for clean transportation fuels and chemical production. Current Fischer-Tropsch facilities are using coal-to-liquid (CTL) and gas-to-liquid (GTL) conversion. It is possible to use any hydrocarbon, solid or gaseous, as feed material for Fisher-Tropsch synthesis. A simple flow sheet of Fischer-Tropsch is shown in Figure 1.1.

Figure 1.1. Process flow diagram of Fischer-Tropsch synthesis.

During the process feed is first transformed into syngas, hence it is called indirect liquefaction [3]. Syngas is a mixture of carbon monoxide (CO) and hydrogen (H_2). The first step of indirect liquefaction (feed-to-syngas) is an energy intensive and most expensive step. The exact ratio of H_2:CO required for Fischer-Tropsch synthesis depends on the Fischer-Tropsch technology and the design of Fischer-Tropsch gas loop. Ideally, there should be a H_2:CO ratio of around 2 in the syngas because this is the ratio in which H_2 and CO is consumed by Fischer-Tropsch synthesis (Eq. 1.1).

$$nCO + 2nH_2 \rightarrow (-CH_2-)_n + nH_2O \qquad \ldots 1.1$$

The H_2:CO ratio in syngas can be adjusted during syngas conditioning by water gas shift (WGS) (Eq. 1.1), methane reforming and gas recycle after Fischer-Tropsch synthesis.

$$CO + H_2O \leftrightharpoons CO_2 + H_2 \qquad \ldots 1.2$$

The types of synthesis are based on type of catalyst used and temperature of Fischer-Tropsch synthesis. The three type of synthesis are iron based high temperature Fischer-Tropsch (Fe-HTFT), iron based low temperature Fischer-Tropsch (Fe-LTFT) and cobalt based low temperature Fischer-Tropsch (Co-LTFT). During Fischer-Tropsch synthesis (Eq. 1.1), syngas is converted into heavier hydrocarbons, water and water-soluble oxygenates, although the latter is not reflected by the simplified reaction equation.

The product formed from syngas by Fischer-Tropsch synthesis is upgraded to produce final products. Less than half of the product after Fischer-Tropsch synthesis is a liquid organic product [3]. Production of synthetic crude oil is accompanied by the production of an aqueous phase product stream called Fischer-Tropsch reaction water, that consists of water and dissolved oxygenates such as alcohols, aldehydes, carboxylic acids, esters and ketones [4].

During Fischer-Tropsch synthesis, water is often the largest product phase. To put this into perspective, approximately 25 - 30 ML (i.e. $2.5\text{-}3.0\times10^7$ L) of Fischer-Tropsch reaction water is produced daily at SASOL SynFuels, Secunda, South Africa [5]. The oxygenates in the Fischer–Tropsch aqueous product are classified as either nonacid chemicals (typically aldehydes, ketones and alcohols) or as acid chemicals (carboxylic acids). Distillation of the Fischer-Tropsch reaction water removes nonacid chemicals leaving behind water-soluble acid chemicals in water as bottom stream. The unrecovered stream of carboxylic acids in water, called acid water, is an effluent and needs to be treated.

2. Objective

The primary objective was to find an alternative technique that not only treats the Fischer-Tropsch reaction water effluent, but can also replace the conventional biological methods being used by current industrial facilities. . An alternative method was sought, because it was unlikely that biological treatment would be cost effective in cold climates. Of particular interest was the future application of Fischer-Tropsch synthesis in Canada.

Three alternative methods were proposed to deal with Fischer-Tropsch acid water:

- Fractional Freezing
- Electrolysis
- Catalytic Decomposition

3. Scope of work

In Chapter 2 literature was reviewed which provided an insight of what has been done till now. Literature specific to the alternatives that were proposed was also reviewed, i.e. Fractional Freezing, Electrolysis and Catalytic Decomposition.

In Chapter 3 the objective was to have a base case to which other techniques can be compared with. A cost estimation of the treatment methods used by industry currently, that is biological method was done. The basis was 100 m^3/h acid water containing 1 wt% carboxylic acids for a plant location in Fort McMurray, AB, Canada.

In Chapter 4, 5 and 6 alternative methods for treatment of Fischer-Tropsch acid water were investigated, namely, Fractional Freezing, Electrolysis and Catalytic Decomposition. Experiments were performed to determine whether the alternative methods are effective in treating Fischer-Tropsch reaction water effluent. Cost evaluation of each method was done taking feed and plant location the same as was for biological method.

In Chapter 7 a comparison of Fractional Freezing, Electrolysis and Catalytic Decomposition was performed with the base case biological method to determine whether these methods can cost-effectively replace the currently practiced biological methods for treating Fischer-Tropsch acid water or not.

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Chapter 2: Literature Review

1. Introduction

In Industry Fischer Tropsch synthesis is used to convert solid or gaseous carbon-based energy sources into products that may be used as fuels or chemicals. However, Fischer Tropsch reaction is just a part of a much larger process. Fischer Tropsch synthesis is a technology used for the conversion of syngas, which is a mixture of carbon monoxide and hydrogen into a synthetic crude oil (syncrude) [1]. Production of synthetic crude oil is accompanied by the production of an aqueous phase products that consists of water and dissolved oxygenates such as alcohols, aldehydes, carboxylic acids, esters and ketones [2].

During Fischer-Tropsch synthesis, water is often the largest product phase. The water rich product stream is called "Fischer-Tropsch reaction water" and is a high strength chemical oxidation demand (COD) petrochemical effluent. Fischer Tropsch wastewater is generated in large volumes, 25% more than hydrocarbon products on weight basis [3]. To put this into perspective, approximately 25 - 30 ML (i.e. $2.5\text{-}3.0\times10^{7}$ L) of Fischer-Tropsch reaction water is produced daily at SASOL SynFuels, Secunda, South Africa [4].

The composition of the Fischer Tropsch reaction water is largely dependent on the catalyst metal used in the Fischer-Tropsch reactor and the reaction conditions (e.g. temperature, pressure) employed, as shown in Table 1 [5].

Table 2.1. Typical organic composition of Fischer-Tropsch reaction water from different Fischer-Tropsch Synthesis operating modes [5].

Component (mass %)	**LTFT** (Cobalt Catalyst)	**LTFT** (Iron Catalyst)	**HTFT** (Iron Catalyst)
Water	98.89	95.7	94.11
Non-acid oxygenated hydrocarbons	1	3.57	4.47
Acidic oxygenated hydrocarbons	0.09	0.71	1.4
Other Hydrocarbons	0.02	0.02	0.02
Inorganic components	<0.005	<0.005	<0.005

Low Temperature Fischer-Tropsch LTFT Cobalt or Iron catalysts

High Temperature Fischer-Tropsch HTFT Iron catalyst

The non-acid oxygenated hydrocarbons are comprised of compounds from the group including: alcohols, aldehydes and ketones, more specifically from the group including: acetaldehyde, propionaldehyde, butyraldehyde, acetone, methyl-propyl-ketone, methanol, ethanol, propanol, butanol, pentanol, hexanol, and heptanol. The acidic oxygenated hydrocarbons are from the group including: formic acid, acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, heptanoic acid, and octanoic acid [5].

Distillation of the reaction water removes non-oxygenated and oxygenated hydrocarbons and yields organic (carboxylic) acid-enriched stream (average COD of 16000 mg/L). When water soluble oxygenates is not recovered the aqueous product stream is an effluent that has to be treated [2]. The effluent stream contains 1 to 1.5 % v/v C_2 – C_4 organic acids (> 85 % acetic acid), as well as C_5- C_{18} organic acids, including light oils, aldehydes, ketones, cresols and phenols [4]. This product is often referred to as acid water. Due to the limitations set by Regulatory Agencies on the COD level in wastewater for effective use and proper disposal into waterbodies, the effluent stream from Fischer Tropsch process needs to be treated. As per Municipal Program Development Branch, Alberta Canada the COD limit in the wastewater should be less than 200 mg/L [6].

2. Current approaches to dealing reaction water (Biological method)

The Fischer Tropsch reaction water effluent in current industrial facilities is treated by biological method (using microorganisms). Biological treatment systems provide good environmental conditions for microorganisms to grow and reproduce under controlled conditions. In return these microorganisms remove organic matter and therefore control the depletion of oxygen in the influent [7].

The industrially applied biological treatment processes includes aerobic treatment and anaerobic treatment methods. The aerobic and anaerobic treatment methods are same as are conventionally used for domestic and industrial wastewater treatment. The aerobic and anaerobic treatment include adding nutrients in the form of nitrogen (e.g. urea, ammonia or ammonium salts) and phosphorus (e.g. phosphate salts) containing compounds to accelerate microbiological degradation of the organic constituents. In addition, pH control using alkali salts such as lime, caustic and soda ash may be required due to the acidity of the water [5].

Anaerobic digestion typically yields methane, carbon dioxide and sludge as by-products apart from water stream. The methane may be released to the environment via an acceptable system (e.g. flare stack) or, preferably, recovered. Recovered methane may be used as a fuel gas, or returned for reforming where a gas reformer is present in the facility. The sludge may be incinerated, used as landfill or as a fertiliser or soil conditioner. Apart from a water-rich stream, aerobic treatment typically yields carbon dioxide and sludge as by-products. The carbon dioxide may be released to the environment. The sludge may be incinerated, used as land fill, fertilizer or soil conditioner. Applications for the purified water produced by the method described above may include its use as cooling water, irrigation water or general process water. The purified water typically has COD in the range of 50-200 mg/L [5].

2.1.Challenges with aerobic digestion of acid water

The successful operation of these activated sludge systems has proven to be difficult with low organic loading rates (3.5 kg COD/m^3.d), low COD removal efficiencies (<80 %) and high specific air requirements (60 - 75 m^3 air/kg COD removed). It is predicted that these operational difficulties can be due to organic shock loadings, variation in volumetric and hydraulic loadings, as well as variations in the composition of the various process streams being treated. As Fischer Tropsch reaction water constitutes 70 % of the COD load on the activated sludge system in a typical facility, there is a need to improve the treatment cost and efficiency of treating the Fischer-Tropsch acid stream [4].

2.2.Challenges with anaerobic digestion of acid water

The microorganisms responsible for metabolizing carboxylic acids in acid water grow at temperatures of around 36 to 44°C and are most effective and efficient in this temperature range [8]. For colder regions, acid water from Fischer-Tropsch synthesis needs to be heated to the temperature at which microorganisms grow, resulting in increase in the operational cost. There is a need for an alternative treatment process when the Fischer-Tropsch needs to be applied in colder regions.

3. Potential alternative approaches

The main challenge in treating Fischer-Tropsch acid water is to remove carboxylic acids from it, so as to get acid free water. This can be done either destroying or by recovering carboxylic acids in acid water. Alternatively, the carboxylic acids can be prevented from forming acid water by converting them upstream.

Potential alternative approaches that can be used to treat Fischer-Tropsch synthesis acid water are as follow:

a. Recovery of carboxylic acids in Fischer –Tropsch acid water was considered as an alternative to the biological method, because the carboxylic acids can be purified and sold as chemicals. A liquid-liquid extraction process using a light solvent in a packed bed extractor can be used to recover carboxylic acid in Fischer-Tropsch synthesis acid water [9]. This strategy was evaluated by Sasol.. It was found that the carboxylic acids could be selectively extracted with 2-methyl-2-methoxypropane (methyl tertiary butyl ether, MTBE). The process was found to be energy intensive and acid water being corrosive, led to materials related problems. This carboxylic acid treatment technology was never taken beyond pilot plant stage [1]. Based on the reported outcome, this method will not be investigated.

b. A case study of recovery of acetic acid from effluent by using fractional freezing was done [10]. Recovery of acetic acid from acetic acid-water solution by ordinary distillation is quite difficult. So the separation was done by fractional freezing and it was found experimentally that large amount of acetic acid (about 71.5%) can be recovered by employing fractional freezing. Another case study for recovery of acetic acid (95% recovery of the acid) from acetic acid-water solution was done taking 83 gal/min of 1% acetic acid in water as feed by using fractional freezing [14]. For this study, there was an energy reduction of about 85% as compared to azeotropic distillation. Therefore, fractional freezing is a technique that could be investigated to treat Fischer-Tropsch synthesis acid water.
c. Electrochemical oxidation of formic acid, acetic acid and oxalic acid in wastewater was investigated by bulk electrolysis using boron-doped diamond electrodes to completely oxidize organics to CO_2 [11]. During the experiment 90% of acetic acid was oxidized to CO_2. Since electrochemical oxidation of carboxylic acids resulted in oxidation of acetic acid to CO_2, this method can be investigated to treat Fischer-Tropsch synthesis acid water.
d. The ketonization of carboxylic acids results in production of ketones. Direct ketonization of acetic acid, propionic acid, hexanoic acid and heptanoic acid was carried out in the gas phase over solid catalysts under flowing condition [23]. It was reported that 97% conversion of acetic acid into acetone using 10wt% CeO_2/SiO_2 at 400°C. This method can be investigated to ketonize the carboxylic acids before condensation, thereby preventing the formation of acid water.
e. A method that is related to (d) and that was not evaluated, is to manipulated the vapor-liquid-liquid equilibrium that leads to dissolution of the carboxylic acids in the water.

4. Fractional freezing for treating acid water

Fractional freezing is a separation technique based on difference in melting points of the components of a solution. Fractional freezing or freeze crystallization can be applied in separation processes to either purify or concentrate a material, depending on the desired end product [12]. It is a process of enriching a solution by partially freezing it, removing frozen material and thus concentrating the solution. One distinguishing feature of fractional freezing is that the phase change process is not isothermal, as in the case of a pure substance; but rather, the freezing occurs over a temperature range within which a solid - liquid two-phase region exists. This class of problem is of interest in the areas of metal processing, preservation of biomaterials, and desalination of sea water [13]. Fractional freezing permits operation in a single theoretical stage as contrasted to the incremental separation and multistage processes needed in vapor-liquid separations. In some applications, freezing can perform a separation with a 75 to 90% reduction of the energy required by conventional distillation-acetic acid and acrylic acid refining are two examples [14]

The solid-liquid equilibrium diagrams of acetic acid and water were investigated and it is shown in Figure 2.1 [15]. In the equilibrium diagram, section I represent the region where there is solution (acetic acid and water) and some ice. Section II represents solution (acetic acid and water) and solid acetic acid. Section III represents homogenous solution of acetic acid and water. The horizontal line is the temperature below which all concentrations are frozen solid. The point at which curve breaks is the eutectic point or temperature at which crystals of both acetic acid and water are formed simultaneously. At eutectic point (-32.5°C), composition of the solution is 41% water. Except at eutectic point, only one component in the solution crystallizes and that crystal is pure [14].

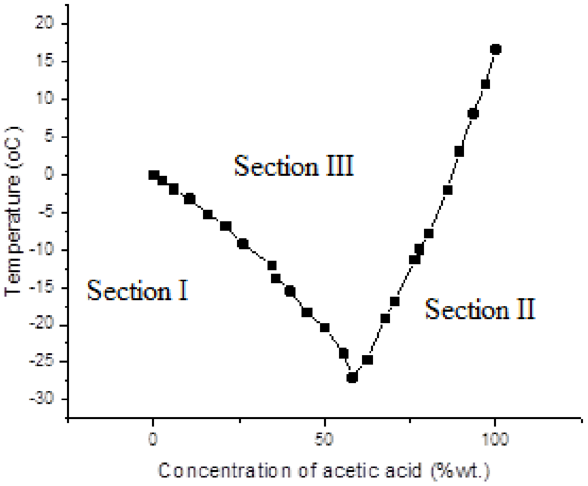

Figure 2.1. Solid-liquid equilibrium diagram for acetic acid and water.

For acetic acid and water solution, the eutectic point is at 59% acetic acid and around -26.66°C. At the eutectic point, the two crystals can be separated very effectively by gravity. The ice (sp. gr. = 0.92) floats in the solution (sp. gr. = 1.03), while the acetic acid crystals (sp. gr. = 1.05) settle to the bottom [14].

To apply fractional freezing to the process of interest, the phase diagrams for the carboxylic acids present in reaction water needs to be known. The phase diagrams will determine at what operating conditions can best be performed. Once the operating conditions have been identified, a total mass balance can be constructed around the system. Process heat loads on the freezers can be calculated from the heat of fusion of the crystallized material, together with the sensible heat load in cooling the process fluid between the inlet and discharge temperatures of that stage.

Unit operations that make up the fractional freezing process are a i) Freezer or crystallizer, where a portion of the liquid is changed to the solid phase by removing heat, ii) a separator where the crystal phase is separated from the remaining liquid, and the crystals are washed to remove adhering solution from the surface, iii) refrigeration cycle that acts like a heat pump removing heat from the freezer and compressing it to a sufficient pressure that it will condense to provide the heat needed to melt the crystal after it has been separated and iv) heat exchangers to recover cold energy [16]. Continuous crystallizers have been the preferred approach, due to the availability of design methods and proven industrial operation. However mechanical complexity and high installed costs make continuous freezing processes too expensive for small-scale water treatment systems [17].

5. Electrolysis for treating acid water

The Kolbe reaction or Kolbe electrosynthesis is anodic oxidation of carboxylic acids. It is not actually an oxidation of the carboxylic acid itself, but rather of its ion [18]. During Kolbe reaction (Kolbe electro-synthesis of hydrocarbons), anodic oxidation of carboxylate structure takes place with subsequent decarboxylation and coupling to yield a hydrocarbon or a substituted derivative corresponding to the alkyl function in the carboxylate reactant. The Kolbe reaction is an organic reaction proceeding on an oxidizing electrode that is an anode. The best known example is the reaction of acetate represented as (Eq. 2.1):

$$2CH_3COO^- \rightarrow C_2H_6 + 2CO_2 + 2e \qquad \ldots 2.1$$

Free radical pathway for the same process wherein direct electrochemical oxidation of the carboxylate ion takes place is shown in Eq. 2.2. Oxidation of the carboxylate is followed by decomposition of the radical to release CO_2 (Eq. 2.3). The remaining alkyl radicals combine to produce a hydrocarbon product (Eq. 2.4) [20]. The total reaction may be written as follows:

$$2RCOO^- \rightarrow 2RCOO^{\cdot} + 2e \qquad \ldots 2.2$$

$$2RCOO^{\cdot} \rightarrow 2R^{\cdot} + 2CO_2 \qquad \ldots 2.3$$

$$R^{\cdot} + R^{\cdot} \rightarrow R - R \qquad \ldots 2.4$$

The radicals in the above reactions are formed in a specifically adsorbed or chemisorbed state at sites upon the metal electrode surface acting as an electro-catalyst for the reaction. It is to be noted that the above mentioned reaction correspond to first-order kinetics [19].

Experimentally, the Kolbe reaction in aqueous solutions usually proceeds with increasing efficiency as the anode potential is raised [20]. A plot of anode potential versus the logarithm of the current density for acetate electrolysis is shown in Figure 2.2. In the low-potential region, oxygen evolution due to oxidation of water is observed up to about + 21 V. At high-potential, anodic oxidation of acetate ion occurs at about +23 V (this is commonly referred to as the critical potential), as evidenced by the formation of almost quantitative amounts of ethane and carbon dioxide, accompanied by small amounts of oxygen [18]. This is one of the most characteristic features of the anodic oxidation of carboxylate ions at platinum anodes: it takes place at a very high positive potential, above +23 V (in actual preparative runs, probably in the region between +25 and +30 V).

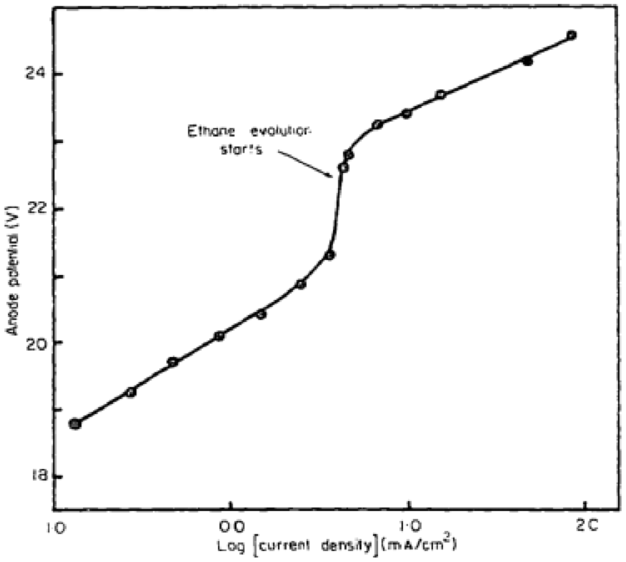

Figure 2.2. Anode potential versus the logarithm of the current density for the electrolysis of 0.5 M aqueous sodium acetate.

In aqueous solution, only a smooth platinum or iridium anode leads to the formation of radical and/or cationic intermediates from carboxylate ions. Gold, nickel, and platinized platinum electrodes give oxygen evolution only. Carbon electrodes result in some products formed via radicals, but the formation of carbonium ions seems to be the predominant reaction [21]. The different behavior of these electrodes is connected with the varying potential at which oxygen is liberated at them. The potential required for the formation of ethane lies below that at which oxygen is evolved at platinum or iridium anodes but above the value for iron and palladium anodes [22].

An increase in temperature tends to decrease the yield of coupling product in those cases which have been systematically investigated. It is not known whether this decrease is accompanied by an increase in the yield of products formed via the carbonium ion path [18].

6. Catalytic conversion of carboxylic acids in vapour phase

The catalytic conversion method of treatment is different from the rest of methods mentioned in this section. This method of treatment is not related to Fischer-Tropsch reaction water, but prevents the carboxylic acids from ending up in the reaction water In this method the carboxylic acids are treated when they are still in the vapor phase after Fischer-Tropsch synthesis and before they being condensed. By destroying the acids before they end up in the reaction water the problem of acid water treatment can be prevented.

Three general routes are associated with the catalytic deoxygenation of carboxylic acids as shown in Figure 3 [23]:

1) Ketonization by C–O bond cleavage to generate ketones, and possibly further hydrogenation to produce alcohols;

2) Decomposition (decarboxylation and decarbonylation) of carboxylic acids by breaking C–C bonds to produce alkanes with one less carbon, CO, and/or CO_2;

3) Hydrogenolysis (HDO): Hydrogenolysis by C–O bond cleavage to produce aldehydes, followed by hydrogenation to form alcohols. These alcohols can be then dehydrated and hydrogenated to yield alkanes, or react with carboxylic acids to form esters.

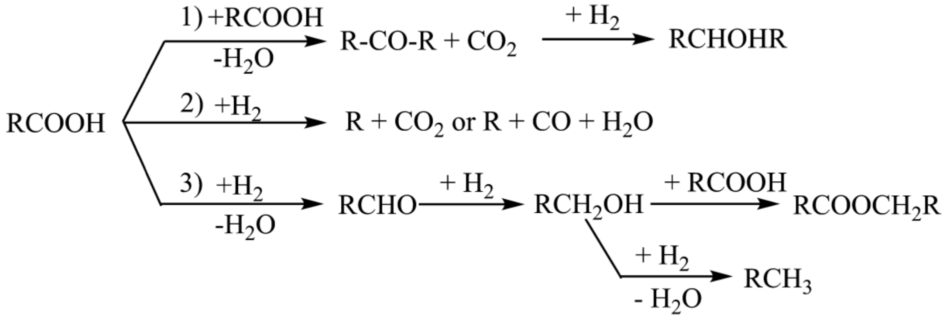

Figure 2.3. Main reaction pathways associated with catalytic deoxygenation of carboxylic acids, R stands for alkyl groups.

Ketonization of carboxylic acids is the only process that will be discussed here. The ketonization reaction of carboxylic acids follows the general equation:

$$2RCOOH \rightarrow R - CO - R + H_2O + CO_2 \qquad \ldots 2.5$$

In the ketonization of carboxylic acids, oxide catalysts are active [23]. Metal oxides supported on inorganic carriers, pumice, alumina, silica and titania or active carbon, have been used in the reaction mentioned above [24]. In one study [24] twenty metal oxide catalysts (10 wt %) supported on SiO_2 were investigated in the ketonization of acetic acid. The reaction temperature was 300–450°C, presented in Table 2.1. At 375 °C, the acetone yield was higher than 50% over the following oxides: MgO, CdO, CoO, Fe_2O_3, La_2O_3, CeO_2, and MnO_2. The loading of metal oxides had a positive effect on the yield of acetone, while Al_2O_3 was found to be the best support to generate a higher yield of acetone than other supports such as SiO_2 and TiO_2.

Table 2.1. Activity of 10 wt% MO_x/SiO_2 catalysts in ketonization of acetic acid. Liquid hour space velocity (LHSV) = 2 cm^3 g^{-1} h^{-1} [24].

Active phase	Yield of acetone (%)						
	573 K	598 K	623 K	648 K	673 K	698 K	723 K
CdO	6	27	73	76	94	-	-
CeO_2	9	24	31	96	97	-	-
Fe_2O_3	13	32	39	66	59	60	52
La_2O_3	3	12	14	50	87	-	-
MgO	7	20	39	53	59	68	74
MnO_2	18	22	34	72	96	-	-

7. Summary

Till now, biological methods have been employed to treat Fischer–Tropsch acid water. The shortcomings of biological treatment, particularly in colder climates, were outlined. The remainder of the literature review focused on the fundamentals of three alternative pathways that were explored to convert carboxylic acids.

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Chapter 3: Biological Method (Base Case)

1. Introduction

Biological treatment process is usually used to treat industrial wastewater effluent. Biological treatment method, apart from being generally less expensive than chemical method, does not produce any effluent harmful to environment [1]. However, biological processes are highly sensitive towards environmental conditions like pH and temperature [2]. Thus, changes in the environmental conditions affect the process efficiency. Biological treatment systems must provide good environmental conditions for microorganisms to grow and reproduce under controlled conditions. In return these microorganisms remove organic matter and therefore control the depletion of oxygen in the influent [3].

There are two classes of processes with which wastewater can be treated biologically:

i) Aerobic method, where microorganisms have access to oxygen;
ii) Anaerobic method, where microorganisms do not have access to oxygen.

Initially only aerobic processes were used to treat the industrial wastewater as anaerobic processes were considered less reliable because less was known about these systems. High cost of aeration in aerobic systems and better understanding of anaerobic systems later resulted in development of interest in anaerobic systems. Anaerobic processes are increasingly being used in the last few decades because of low sludge production, removal of higher organic loading, high pathogen removal, methane gas production and low energy consumption [4].

As was pointed out in Chapter 2, the Fischer–Tropsch reaction water contributes 70% chemical oxygen demand (COD) load of a typical facility, with an average COD varying between 12000 mg/L to 22000 mg/L. A cost evaluation of both aerobic and anaerobic processes was done; so as to compare new techniques, refer to chapter 7, to the biological method to determine whether new techniques can replace conventional biological treatment methods. For this evaluation the COD of the treated water had to be <200 mg/L and <100 mg/L of total suspended solids (TSS) as per Alberta Canada regulations [5].

All costing was performed for a Fort McMurray, AB, Canada plant location. The feed basis was 100 m^3/h acid water with an acid concentration of 1 wt%.

2. Process description of biological methods

2.1. Aerobic activated sludge system

Activated sludge (AS) is commonly used biological treatment process for treatment of sewage and industrial waste. Activated sludge is an example of suspended system, consisting of microorganisms suspended in the wastewater, wherein wastewater is mixed with biological solids, that is microorganisms, which are held as suspension by agitation. These microorganisms metabolize the organic matter, present in the wastewater, producing microbial biomass and carbon dioxide. The microorganisms grow at near neutral pH of about 6.5 to 8 [2]. Operating parameters like temperature, concentration of organic compounds in wastewater and pH greatly influence the treatment process. As long as a suitable environment is provided, microorganisms are able to degrade the oxidisable material in the wastewater. Aerobic conditions must be maintained in the reactor for growth of microorganism. A general process diagram for activated sludge is shown in Figure 3.1.

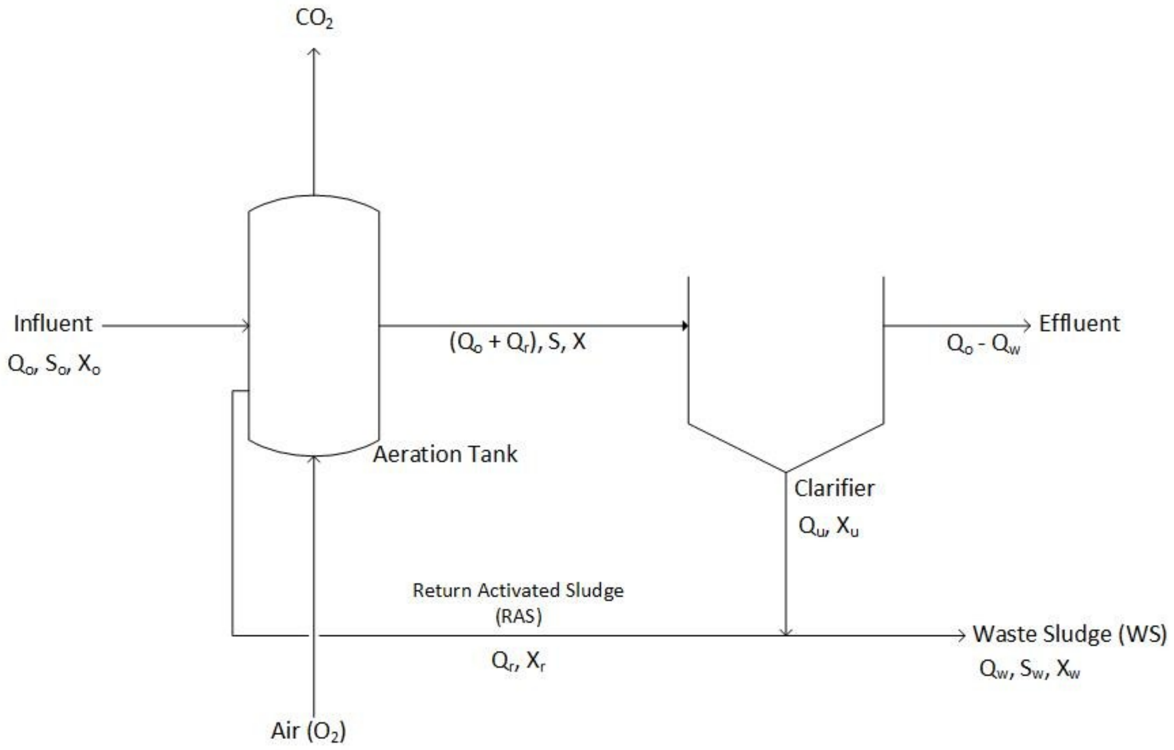

Figure 3.1. Activated Sludge Process Diagram.

The outlet of aeration tank is called mixed liquor consisting of wastewater and solids (biological mass). This mixed liquor is discharged to clarifier where solids are separated from wastewater. The separated solid, i.e. sludge is mixed with the influent, all or part of it, and is fed to the aeration tank. Excess sludge is removed as waste sludge.

The activated sludge flocs act as a strong coagulant, resulting in the removal of particulate organic material by physical processes, the sludge flocs can capture the particles by screening, enmeshment or adsorption, making them part of the solid (sludge) phase. These physical processes remove the particles. It will accumulate in the solid phase, until it is discharged as part of the excess sludge [6].

2.2. Anaerobic system

In anaerobic process organics in wastewater are broken down by microorganisms, without aid of oxygen, producing methane, carbon dioxide and biomass as final products. Anaerobic microorganisms use the oxygen that is in the oxides introduced into the system or from the organic material in the wastewater [7].

$$organics + combined\ O_2 \xrightarrow{anaerobic\ microbes} new\ cells + CH_4 + CO_2 + \ residue$$

Sources of combined O_2: $CO_3^{2-}, SO_4^{2-}, NO_3^-, PO_4^{3-}$ [3]

Anaerobic system differs from aerobic system in two ways, i) providing oxygen (from air) for microorganism growth is not required, and ii) during the decomposition of organics in wastewater biogas is also produced. Biogas is produced when anaerobic microorganism feed on biodegradable material. Biogas is a mixture of methane (around 60%) and carbon dioxide (around 30%) [8]. Methane being a source of energy, can be stored and used for energy production, which in turn can be used to provide power and heat for the process of anaerobic digestion.

Anaerobic systems are greatly affected by temperature. Low temperatures cause relatively longer generation time of anaerobic bacterial populations, lower biochemical activity and thus decrease in biogas yield [9]. Anaerobic digestion can be carried out in two conventional temperature levels determined by species of methanogens (methane producing microorganisms), i) thermophilic, where digestion in the tank is carried out at around 55^{o}C, it has shorter retention time but more expensive in terms of energy consumption for heating sludge, ii) mesophilic, where digestion in the tank is carried out at around 36^{o}C, it has longer retention time and is less expensive as compared to thermophilic [1].

2.3. Design equations

Mass balance over biomass production

Influent + production = effluent + sludge waste

$$Q_oX_o + V\frac{dX}{dt} = (Q_o - Q_w)X_e + Q_wX_w \quad \text{...3.1}$$

Or

$$\mathrm{Q_oX_o} + \mathrm{V}\left(\frac{\mathrm{\mu_mS}}{\mathrm{K_s+S}}\mathrm{X}\text{-}\mathrm{K_dX}\right) = (\mathrm{Q_o}\text{-}\mathrm{Q_w})\mathrm{X_e} + \mathrm{Q_wX_w} \quad \text{...3.2}$$

Mass balance over substrate

Influent - consumption = effluent + sludge waste

$$Q_oS_o - V\frac{dS}{dt} = (Q_o - Q_w)S_e + Q_wS_w \quad \text{...3.3}$$

Or

$$Q_oS_o - \frac{V}{Y}\left(\frac{\mu_m SX}{K_s+S}\right) = (Q_o - Q_w)S_e + Q_wS_w \qquad \ldots 3.4$$

Where,

$\frac{\mu_m S}{K_s+S}$ = Monods equation for growth of microorganisms without inhibition.

Q_o, Q_w = Influent and waste flow rate, m^3/d

X_o, X, X_e, X_w = Biomass in influent, bioreactor, effluent and waste, mg/L

V = Fluid volume in aeration tank, m^3

μ_m = Maximum specific growth rate, d^{-1}

S = Substrate concentration in bioreactor, mg/L as COD

K_d = Microorganism death rate, d^{-1}

Y = Yield factor, mg biomass produced/mg food consumed

K_s = Half saturation constant, mg/L

S_o, S_e, S_w = Substrate in influent, effluent and waste, mg/L as COD

Assumptions:

1. Influent and effluent biomass concentrations are negligible.
2. Assume that no biochemical action takes place in clarifier.

Therefore above equations become

$$\frac{\mu_m S}{K_s+S} = \frac{Q_w X_w}{VX} + K_d \qquad \ldots 3.5$$

$$\frac{\mu_m S}{K_s+S} = \frac{YQ_o}{VX}\left(S_o\text{-}S\right) \qquad \ldots 3.6$$

On combining both equations, overall mass balance

$$\frac{Q_w X_w}{VX} + K_d = \frac{YQ_o}{VX}\left(S_o\text{-}S\right) \qquad \ldots 3.7$$

$$\frac{Q_o}{V} = \frac{1}{\theta} \qquad \ldots 3.8$$

$$\frac{Q_w X_w}{VX} = \frac{1}{\theta_c} \qquad \ldots 3.9$$

Where,

θ = Hydraulic retention time = $\frac{\text{capacity of fermenter } (m^3)}{\text{fresh substrate added daily} (m^3/d)}$

θ_c = Solid retention time = $\frac{\text{mass of organisms in the aeration (mg/L)}}{\text{mass of organisms remove daily (mg/L)}}$

On substitution and rearranging

$$X = \frac{Y\theta_c}{\theta(1+\theta_c K_d)}(S_o\text{-}S) \qquad \ldots 3.10$$

Food to microorganism ratio

$$\frac{F}{M} = \frac{S_o\theta}{X} = \frac{S_o Q_o}{XV} \qquad \ldots 3.11$$

Where,

$F: M$ = Food to microorganism ratio.

3. Results

3.1. Design basis

Acid water, which is the acid enriched effluent stream from a Fischer Tropsch process, was used as feed material. For the designs this feed material was available at temperature of 25°C and atmospheric pressure. The feed basis was 100 m^3/h acid water with an acid concentration of 1wt% with the following composition: 0.70 ethanoic acid, 0.15 propionic acid, 0.10 butyric acid and 0.05 pentanoic acid.

Following assumptions were made for calculating costs:

1. Natural gas price of US$5/GJ for generating electricity and for on-site conversion to electricity efficiency of 40% was assumed.
2. Plant location Fort McMurray, AB, Canada, the location factor 1.60 [10]
3. Plant life of 20 years with on-stream factor of 95%.
4. The cost is reported in US dollars.
5. All costs were scaled for inflation to a 2013 cost basis using a cost index for 2004 of 400 and for 2013 of 480 [11].
6. Capital and utility costs were estimated using estimation methods from literature [11].
7. Average summer temperature 20°C and average winter temperature -20°C [12].
8. The discount rate, which is important for comparing the value of money that is available now (and can be reinvested) with money that will become available at some time in the future, is taken as 0% for the ease of comparison.

To normalize the purchasing value of currency to the same point in time, money earned or spent in different years is multiplied by discount factor to adjust for the difference in purchasing power. The interest rate used in discounting future value is known as discount rate. The discount factor allows the conversion of all money flows to be discounted to a single point in time. Appropriate interest factors are applied depending on how and when the cash flow enters a venture. They may be instantaneous, as in the purchase of capital equipment, or uniform, as in operating expenses. It is unrealistic to use 0% discount interest, but for the ease of calculations, in this study discount interest was nevertheless taken as 0%. The main effect of this on the comparison is to introduce a slight bias in favor of higher capital than operating expenses.

3.2. Aerobic treatment system

3.2.1. Process description

Wastewater from Fischer Tropsch process, which is 1wt% dilute carboxylic acid solution, cannot be discharged directly into the water bodies, because of its high COD and acidity. Here we consider the use of an aerobic process to degrade the organic matter present in the acid water so that the treated water can be discharged into water bodies, as shown in Figure3.1. A general description of the operation is as follows: The pump (P-101) lifts the wastewater to the aeration tank R-101. The biochemical reaction for degradation of organic matter present in wastewater takes place at around 20°C and above. As feed is at 25°C and microorganisms can grow at this temperature, there was no need of decreasing the temperature of the feed. An aeration tank (R-101), which acts as bioreactor, is where biomass present in the tank converts the organics in wastewater into carbon dioxide. The aeration tank provides the place for the biomass to be gently mixed with the incoming wastewater and provide a stable environment for the biomass to thrive and grow. The biomass is a varied group of aerobic microorganisms, which utilize the organics and nutrients and reproduce. For the microorganisms to grow and reproduce, nutrient mixture, which is the source of nitrogen, phosphorous, magnesium, sulphur, calcium and iron, is added to the aeration tank. During winter because of low ambient temperature, heat was lost from the aeration tank to atmosphere. To maintain the temperature of the tank at which microorganisms grow, heating was done by steam. A blower (B-101) provides aeration tank with adequate air for proper mixing and air (oxygen in it) to be used by microorganisms. The clarifiers (R-102) are large settling tanks. Using the fact that biomass is heavier than the water, the biomass settles at the bottom of the tank and is removed by the pump (P-103) and a part is returned back to aeration tank by using another pump (P-102). Optionally the treated water that may be at higher temperature can be used to raise the temperature of inlet wastewater. Treated water is pumped (P-104) from the clarifier to heat exchanger (HE 101).

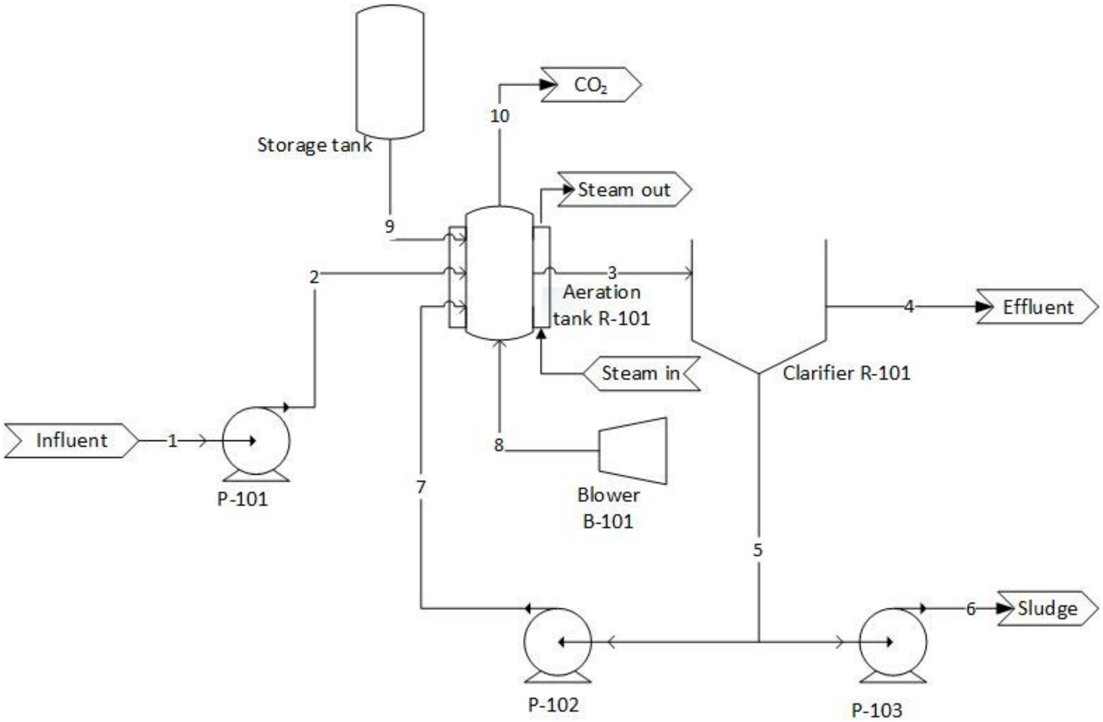

Figure 3.2. Process flow sheet of Aerobic treatment system.

3.2.2. Material balance

Material balance was done for aerobic treatment system as per Figure 3.1. The principle thing that was dealt with was COD in Fischer-Tropsch reaction water effluent. The COD in influent was 18000 mg/L [1] and with the process of efficiency of 98.9%, COD in effluent was 200 mg/L. Around 50-90% of clarifier bottom is returned to aeration tank. Return activated sludge flow rate was calculated by following equation:

$$RAS = \frac{Solids\ in\ MLSS}{Solids\ in\ RAS - Solids\ in\ Solids} \times Influent\ flow\ rate \qquad \ldots 3.12$$

Clarifier underflow contains around 5-8% solids and around 8000 to 10000 mg/L [13]. Total dissolved solids in clarifier outlet should be <100 mg/L [5]. Upto 10% of clarifier underflow is disposed off as waste sludge [6].

Following general assumptions were made for Table 3.1:

1. Specific air requirement = 70 m^3air/kg COD removed [1].
2. Microorganism added yeast, 54 mg/L [7].
3. No solids present in influent.

Table 3.1. Material balance over aerobic system with feed 100 m^3/h of 1wt% carboxylic acid aqueous solution having 18000 mg COD/L (Figure 3.2).

Stream	Flow (t/h)	Flow (m^3/h)	Solids (kg/m^3)	Temperature (^oC)
1	100	100	-	25
2	100	100	-	25
3	144.83	144.00	2.8	25
4	97.16	97.16	0.1	20
5	47.66	46.84	8.4	25
6	2.84	3.75	8.4	20
7	44.82	43.10	8.4	20
8	-	$4x10^3$ m^3 air/h	-	-
9	$5x10^{-5}$		-	-
10	2.61		-	-

3.2.3. Energy balance

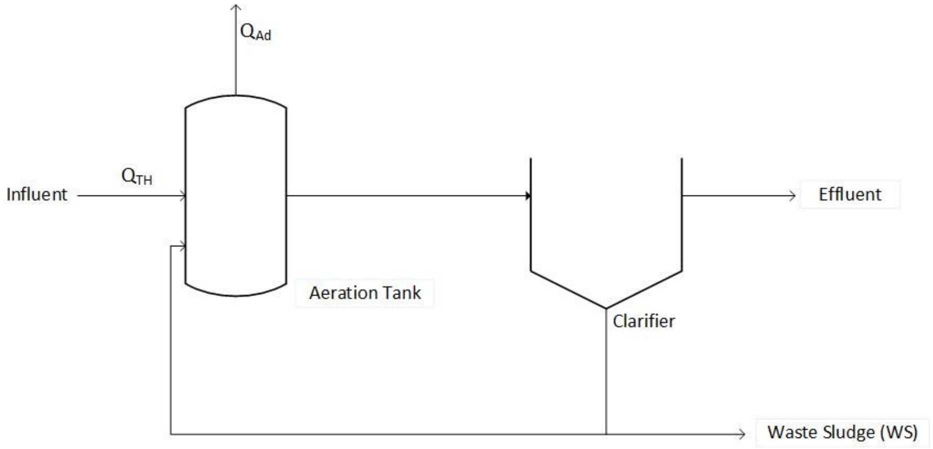

Figure 3.3. Block diagram of aerobic treatment system where Q_{TH} amount of energy is supplied to the system and Q_{Ad} is lost.

Following equation was used was used for energy balance:

$$Q_r = Q_{Th} + Q_{Ad} \qquad \ldots 3.13$$

Where,

Q_r = Total heat required (J/m^3)

Q_{Th} = Heat required for raising the temperature of feed to required temperature (J/m^3)

Q_{Ad} = Heat lost to atmosphere (J/m^3)

For values of Q_r, Q_{Th} and Q_{Ad}, refer Table 3.2.

Since feed is already at 25°C temperature and aerobic process takes place at above 20°C, there is no need of heating the feed solution. Therefore, in Eq. 3.1 Q_{Th} will be zero. The reactor temperature was maintained above 20°C.

In winters, steam at pressure of 8 bars was used to maintain the temperature of reaction mixture at required temperature, which is 20°C.

It was assumed, by the time effluent is discharged and returns activated sludge reaches to reactor back, their temperature decreases to 20°C.

Table 3.2. Energy balance over aerobic treatment system with feed 100 m^3/h of 1wt% carboxylic acid aqueous solution. Plant location Fort McMurray Canada, average summer temperature 20°C and average winter temperature -20°C.

	Aerobic
	Winter
Flow rate, m^3/hr	100
Feed temp (°C)	25
Temp in tank	20
Volume of tank, m^3	500
Specific heat, C_P (kJ/kg.K)	4.18
Heat lost to ambient	
U, (kW/m^2K)	11.3
Ambient temp., (°C)	-20
Temp difference	40
Heat lost, $\boldsymbol{Q_{Ad}}$ (MJ/m^3)	4.6
Total heat required, (MJ/m^3)	4.6
Total heat required, $\boldsymbol{Q_r}$ (GJ/m^3)	**0.005**

Total heat required for aerobic process at 20°C for 100 m^3/h of 1 wt% Fischer-Tropsch effluent was 5 MJ/m^3.

3.2.4. Capital and Operating Cost

To determine the capital cost of each equipment, several critical cost parameters like area of reactor and clarifier and shaft power of blower were predesigned first. From the predesign, purchase cost of each item of equipment (C_P) was determined for the year 2013. Lang factor of 3 was multiplied to purchase cost of each equipment to cover other cost associated with purchase cost like transportation, foundation, piping, insulation, etc. Base bare module factor (F_{BM}), which is special correction factor for extreme conditions, was determined from the material of equipment and its working pressure [11]. Installed cost of equipment (C_{BM}) was calculated by multiplying C_P and F_{BM}. Finally total capital cost for treating per m^3 of Fischer-Tropsch reaction water effluent was calculated by summing up all the cost.

Size of reactor was calculated from the conversion (0.989) of COD inlet (COD of acetic acid=1.07 mg COD/mg acetic acid).

Table 3.3 shows the capital cost summary of aerobic treatment method. The capital cost expressed as an equivalent cost per m^3 acid water treated is \$ 1.259/m^3.

Operating cost was determined as follows:

a. Calculating the cost of amount of microorganisms required per m^3
b. Calculating cost of nutrients required for the growth of microorganism
c. Cost of chemicals required to maintain the pH of the reaction mixture
d. Cost of electricity required for clarifier (scraper) and blower based on their wattage.
e. Cost of steam required to heat the solution in the aeration tank.

Table 3.4 shows the operating cost for aerobic treatment method. The operating cost for treatment of 1 wt% carboxylic acid aqueous solution by the aerobic treatment process is \$0.43/m^3 in summer and \$0.45/m^3 in winter. The slightly higher treatment cost in winter is due to additional heating required.

Table 3.3. Capital cost summary of aerobic and anaerobic treatment system with feed of 1wt% carboxylic acid aqueous solution fed at 100 m^3/h rate. Plant location Fort McMurray Canada, currency US dollars, year 2013. Lang factor 3 and cost index for year 2004 and 2013 used 400 and 480, respectively.

Equipment Identification	**Number**	**Capacity or size specifications**	**Purchased equipment cost (base material)**		**Material factor, F_M**	**Pressure or other factors, F_P**	**Actual bare module factor, F^a_{BM}**	**Actual bare module cost, C^a_{BM}**	**Total (million $)**
			2004	2013					
Reactor (Aerobic) [13]	R-101	785960 m3, 1 atm	$1.6x10^6$	$1.9x10^6$				$1.9x10^6$	5.832
Reactor (Mesophilic)	R-101	785960 m^3, 1 atm	$2.2x10^6$	$2.6x10^6$				$2.6x10^6$	7.92
Reactor (Thermophilic)	R-101	246000 m^3	$1.7x10^6$	$2.0x10^6$				$2.0x10^6$	6.12
Suspended bio carriers		filled till 40% volume of reactor	20000					20000	0.024
Support (sand)		filled till 10% volume of reactor	3925					3925	
Blower	B-101	Centrifugal, Carbon steel, 163 kW shaft power	$7x10^5$	$8.4 x10^5$	-	-	2.5	$2.1 x10^6$	6.341
Clarifier	R-102	8 m ID	$7x10^4$	$8.4 x10^4$	-	-	3	$2.5 x10^6$	0.756
Heat exchanger	HE-101	122 m^2, Shell and tube, Stainless steel, 1 atm	$9x10^3$	$1.1 x10^4$	3	1	6	$6.5 x10^4$	0.194
Heat exchanger	HE-102	137 m^2, Shell and tube, Stainless steel, 1 atm	$1x10^4$	$1.2 x10^4$	3	1	6	$7.2 x10^4$	0.216
Pump	P-101	Centrifugal, Stainless steel, 11.68 kW shaft power	$9.0x10^3$	$1.1 x10^4$	2	2	8	$8.6 x10^4$	0.259
	P-102							$8.6 x10^4$	0.259
	P-103							$8.6 x10^4$	0.259
	P-104							$8.6 x10^4$	0.259
Biogas collector		4 m ID, 40 m vertical, Carbon steel, 2 atm	$1.2x10^5$	$1.5 x10^5$	1	1	4.2	$6.3 x10^5$	1.890

		Aerobic	**Mesophilic**	**Thermophilic**
Total bare module cost (million $)	C_{TBM}	13.658	18.378	16.578
Total module cost (million $)	$C_{TM} = C_{TBM}x1.18$	16.116	21.686	19.562
Auxiliary cost (million $)	$C_A=C_{TM}x0.30$	4.835	6.506	5.868
Total capital cost (million $)	$C_T = C_{TM}+ C_A$	20.951	28.191	25.453
Equivalent capital cost over 20 years plant life with stream factor of 95% ($ per m^3 treated) [a]		1.259	1.694	1.528

[a] The capital cost was converted to an operating cost in $ per m^3 feed processed, assuming a discount rate of 0%.

Table 3.4. Operating cost summary for aerobic treatment system for treating 100 m^3/h of 1wt% carboxylic acid aqueous solution. Feed temperature 25°C. Plant location Fort McMurray Canada, currency US dollars and natural gas price US$5/GJ, steam used for heating at 8 bar pressure.

Operating Cost		Cost ($/m^3)	
Reactor inoculated by yeast	54 mg/l	0.216	
Total Nutrients added		0.129	
pH control	800 mg/l	0.06	
Cost of electricity used by clarifier	0.75kW	0.0001	
Cost of electricity used by Blower	70 m^3 air/kg COD removed=0.1361 m^3 air/m^3.min, 163kW	0.02934	
		Summer	**Winter**
Cost of heating in aeration tank, $/m^3		0	0.019
Total operating cost, $/m^3		**0.434**	**0.453**

Air at the rate of 70 m^{3}air/kg COD removed was used for aeration by using blower.

Therefore, total cost of treatment of 1wt% carboxylic acid aqueous solution by aerobic treatment process is $1.689/m^3 for summer and $1.709/m^3 for winter.

3.3. Anaerobic treatment system

3.3.1. Process description

Process for anaerobic system differs from aerobic system in the temperature of the aeration tank. For anaerobic method temperature of feed at 25°C was raised to 55°C for thermophilic process and to 36°C for mesophilic process by passing feed through heat exchangers. Figure 3.3 shows the process flow sheet of anaerobic process. In heat exchanger HE-101, temperature of feed was increased by using effluent at higher temperature from clarifier. Pump P-104 was used to transfer the effluent from clarifier to HE-101. Heated feed then entered heat exchanger HE-

102 to further increase its temperature. HE-101 was not used for mesophilic process as temperature of effluent was at same temperature as feed. In the aeration tank, biomass present converts organics into biogas (a mixture of carbon dioxide and methane), which was stored in biogas collector. Some of the biogas generated during the process was circulated back, by using a blower (B-101), to the aeration tank for proper mixing. Since biogas contains methane, it can be used as a source of energy for the system. Volume of aeration tank for thermophilic process was less than mesophilic process because temperature in the aeration tank for themophilic process was high and therefore the retention time of solution in the aeration tank was less.

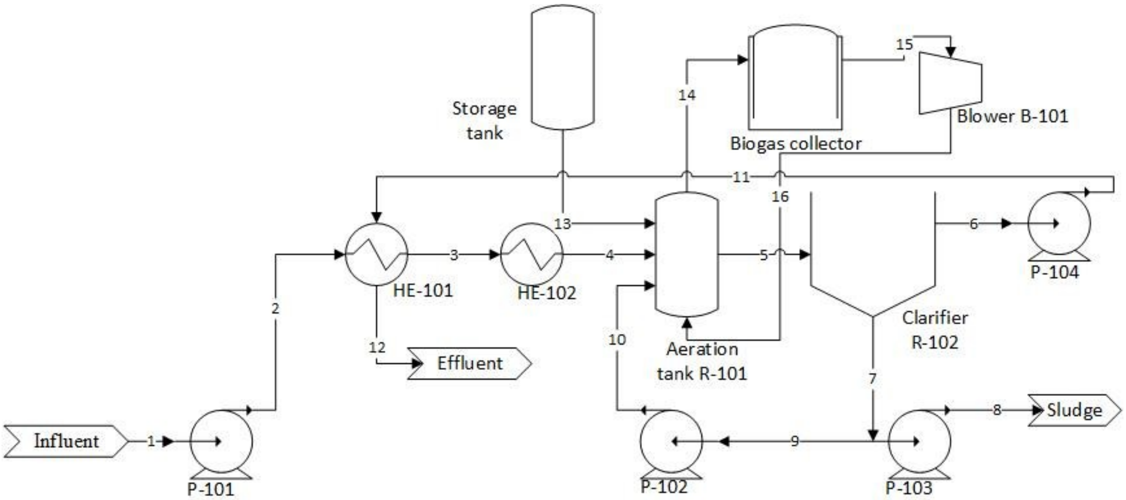

Figure 3.4. Process flow sheet of Anaerobic treatment system.

3.3.2. Material balance

For anaerobic treatment system, a large fraction of the digested organic matter is converted into biogas [6]. A part of biogas produced is circulated back to aeration tank for proper mixing. Following general assumptions were made for Table 3.5:

1. Microorganism added yeast, 54 mg/L [7].
2. Biogas recirculated back was 20% of biogas produced.
3. No solids were present in influent.

Table 3.5. Material balance over anaerobic system with feed 100 m^3/h of 1wt% carboxylic acid aqueous solution having 18000 mg COD/L.

Stream	Flow (t/h)	Temperature (°C)		Suspended Solid (kg/m^3)
		Thermophile	Mesophile	
1	100	25	25	-
2	100	25	25	-
3	100	35	36	-
4	100	55	35	-
5	144.83	55	36	2.8
6	97.16	55	36	0.1
7	47.66	55	36	8.4
8	2.84	45	25	8.4
9	44.82	55	36	8.4
10	44.82	55	36	8.4
11	97.16	45	25	-
12	97.16	34.93	14.9	-
13	5.4×10^{-5}	40	30	0.054
14	0.50	55	36	-
15	0.08	55	36	-
16	0.08	55	36	-

3.3.3. Energy balance

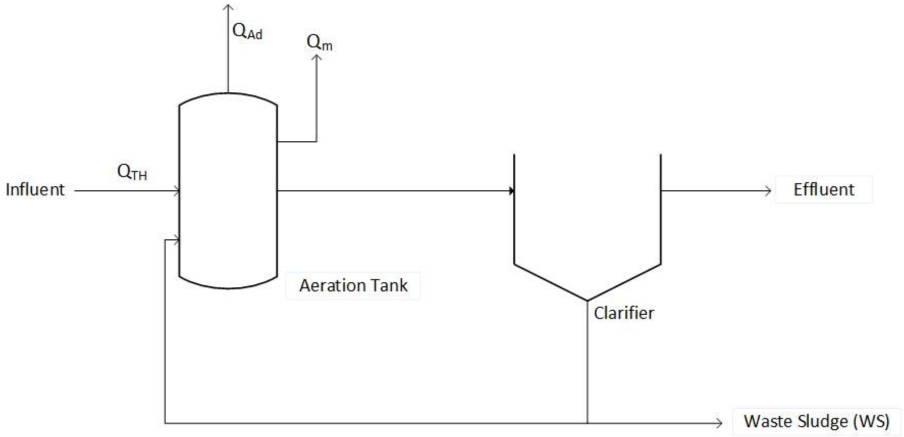

Figure 3.5. Block diagram of anaerobic treatment system where Q_{TH} amount of energy is supplied to the system, Q_{Ad} is lost and Qm is recovered in the form of methane.

Following equations were used for energy balance:

$$Q_r = Q_{Th} + Q_{Ad} \qquad \ldots 3.14$$

$$Q_m = C \times V_m \qquad \ldots 3.15$$

Where,

Q_r = Total heat required (J/m^3)

Q_{Th} = Heat required for raising the temperature of feed (J/m^3)

Q_{Ad} = Heat lost to atmosphere (J/m^3)

Q_m = Energy value of methane (J/m^3)

C = Lower calorific value of methane (kJ/kg)

V_m = Volume of methane generated (m^3/day)

Heat exchangers HE-101 and HE-102 were used to raise the temperature of feed to the temperature required for process (mesophilic = 36°C, thermophilc = 55°C). Steam at 8 bar pressure was used to maintain the reaction mixture at the required temperature.

For mesophilic process, heat exchanger HE-101 was not used as the temperature of clarifier outlet was same as feed temperature. Hence, feed was directly feed to HE-102.

It was assumed by the time effluent reached HE-101, its temperature decreased to 25°C for mesohphic process and 45°C for thermophilic process. Same temperature drop was considered for waste sludge.

For calculations, it was assumed 1kg of COD gives 0.35 m^3 of methane [14].

Energy recovered during anaerobic process in the form of methane was calculated as:

1 m^3 methane = 10 kWh.

623 m^3/h × 0.8 (efficiency) × 10 kWh × 0.4 (electricity conversion efficiency) = 47.85 MWh-e/day.

CO_2 reduction was calculated as:

Coal powered electricity plant: 0.86 Ton CO_2/MWh-e.

47.85 MWh-e/day ≈ 41 Ton CO_2 reduction/day (coal).

Removal of 1 kg COD by conventional aerobic technologies like activated sludge costs about 1 kWh-e [15]. Thus there is energy gain in using anaerobic method.

For values of Q_r, Q_{Th}, Q_{Ad} and Q_m, refer Table 3.6.

Table 3.6. Energy balance over anaerobic treatment system with feed 100 m^3/h of 1wt% carboxylic acid aqueous solution. Plant location Fort McMurray Canada, average summer temperature 20^{o}C and average winter temperature -20^{o}C.

	Thermophilic		**Mesophilic**	
	Summer	Winter	Summer	Winter
Flow rate, m^3/hr	100	100	100	100
Feed temp (^{o}C)	25	25	25	25
Temp in tank	55	55	36	36
Volume of reactor (m^3)	300	300	500	500
Specific heat, C_p (kJ/kg K)	4.18	4.18	4.18	4.18
For Heat Exchanger HE-101				
Hot temp inlet, (^{o}C)	45	45		
Hot temp outlet, (^{o}C)	34.93	34.93		
Cold temp inlet, (^{o}C)	25	25		
Cold temp outlet, (^{o}C)	35	35		
Q, (MJ/m^3)	37.6	37.6		
Heat exchanger area, m^2	123	122		
For Heat Exchanger HE-102				
Feed temp, (^{o}C)	35	35	25	25
Temp difference	20	20	11	11
Heat required, Q_{TH} (GJ/m^3)	0.084	0.084	0.046	0.046
Heat lost to ambient				
U, (kW/m^{2}K)	11.3	11.3	11.3	11.3
Ambient temp., (^{o}C)	20	-20	20	-20
Temp difference	35	75	16	56
Heat lost, Q_{AD} (MJ/m^3)	2.85	6.11	1.83	6.39
Total heat required, Qr (GJ/m^3)	**0.124**	**0.127**	**0.0478**	**0.052**
Methane generated, m^3/h	623			
Biogas generated, m^3/day	1 x10^3			
Lower calorific value of methane, kJ/kg	5x10^4			
Energy value of methane produced, **Qm (GJ/m^3)**	0.205			

3.3.4. Capital and operating cost

Steps for determining capital cost have already been outlined. Additional equipment were used for anaerobic process, like heat exchangers and biogas collector. Capital cost for these equipment were determined the same way.

Since temperature for thermophilic process is high, retention time of wastewater in the reactor is less; therefore size of reactor is small as well. In the capital cost estimation, size of thermophilic reactor was taken 0.313 times mesophilic, based on their rate constant [16].

Capital cost summary for anaerobic process are presented in Table 3.3. The capital cost expressed as an equivalent cost per m^3 acid water treated is $\$1.694/m^3$ for mesophilic and $\$1.528/m^3$ for thermophilic processes.

Operating cost was calculated same way as was for aerobic method. For anaerobic method cost of heating in HE-102 was calculated as well. Steam at pressure 8 bar was used for heating in HE-102 (Table 3.7).

Table 3.7. Operating cost summary for anaerobic treatment system for treating 100 m^3/h of 1wt% carboxylic acid aqueous solution. Feed temperature 25°C. Plant location Fort McMurray Canada, currency US dollars and natural gas price US$5/GJ.

Operating Cost		**Cost ($\$/m^3$)**			
Reactor inoculated by yeast	54 mg/l				0.216
Total Nutrients added					0.129
pH control	800 mg/l				0.06
Cost of electricity used by clarifier	0.75kW				$1\ x10^{-4}$
Cost of electricity used by Blower	20kW				$4x10^{-3}$
		Thermophilic		**Mesophilic**	
		Summer	Winter	Summer	Winter
Cost of heating in HE-102, $\$/m^3$		0.179	0.173	0.096	0.096
Cost of heating in aeration tank, $\$/m^3$		0.017	0.019	0.020	0.019
Total operating cost, $\$/m^3$		**0.605**	**0.613**	**0.528**	**0.537**

Therefore, total cost of treatment of 1wt% carboxylic acid aqueous solution by anaerobic thermophilic treatment process is \$2.133/m^3 for summer and \$2.141/m^3 for winter and for anaerobic mesophilic treatment system is \$2.222/m^3 for summer and \$2.231/m^3 for winter.

4. Discussion

Organic (carboxylic) acid enriched effluent stream from Fischer Tropsch reaction is currently being treated either in activated sludge system, which is an aerobic system, as in SASOL South Africa or in anaerobic system as in PetroSA South Africa. Both, anaerobic and aerobic systems are highly sensitive towards environmental conditions like pH and temperature, changes in which affect the efficiencies of the processes considerably.

The capital cost of aerobic process is less compared to the anaerobic process. However, for the aerobic process the cost of aeration is high. Successful operation of activated sludge systems has proven to be difficult with low organic loading rate (3.5 kg COD/m^3 d), low COD removal efficiency (80%) and high specific air requirements (60-75 m^3 air/kg COD removed) [1]. On the other hand, anaerobic system needs no aeration, therefore, no aeration cost but the capital cost for this treatment system is high. High temperature requirement by the anaerobic system (thermophilic) increases the operational cost in terms of heating the wastewater. However, due to high temperature, retention time is less and thus size of reactor is smaller. For the anaerobic system, biogas is also generated during the process, which could be used to provide power to the system and will result in CO_2 reduction as well.

5. Conclusion

Cost evaluation of biological method was done to keep it as a base case to which other techniques of treatment of 1wt% carboxylic acid aqueous solution can be compared with. Two processes were considered. The first was aerobic process and the second was anaerobic process. From this work, it can be concluded:

a. Cost of treatment of 1wt% carboxylic acid aqueous solution by microbial method was in the range of around \$1.7 to \$2.2/m^3 depending on whether an aerobic process or anaerobic process was used.

b. Temperature of the solution should be in the range in which microorganisms grow, around 20°C for aerobic process and around 36 to 55°C for mesophilic anaerobic and thermophilic anaerobic process because temperature affects the growth of microorganisms and thus efficiency of the process.

c. For colder regions where ambient temperature is below 20°C, temperature of feed wastewater needs to be heated to the temperature at which microorganisms grow which in turn increase operational cost. Therefore, for colder regions cost of treatment is higher.

d. For anaerobic process, 10.38 m^3 biogas was generated per m^3 of wastewater treated. As biogas contains around 60% methane and has energy value of 36MJ/m^3 methane, it can be used as source of energy for the treatment system. At the same time, using biogas as source of electricity results in reduction of CO_2 generation as use of conventional electricity form coal fired plant will be reduced.

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Chapter 4: Fractional Freezing

1. Introduction

Freeze crystallization has been used to separate a wide variety of contaminants from water, such as dissolved minerals, organic chemicals and particulates. Fractional freezing is a separation technique that relies upon solid-liquid phase transition and enables multicomponent mixtures to be split into narrow fractions, ultimately leading to good purity of selected components, through the virtue of selectivity found in solid liquid equilibria [1]. Freeze crystallization can be applied in separation processes to either purify or concentrate a material, depending on the desired end product. As the solvent crystallizes, the solute is concentrated in the remaining liquid solvent. The purified crystals are removed from the impurity-laden liquid (for example by gravity, filtration or centrifuging) and may be used in the solid phase or melted for use as a refined liquid. In some applications, the concentrated liquid may be the desired end product [2], such as fruit juice concentrate.

Purification by evaporation is energy intensive, yet, due to its versatility distillation is ubiquitous in industry. The heat of fusion of ice (6.01 kJ/mol) is six times less than the heat of evaporation of water (40.65 kJ/mol). Hence the energy required to separate water as ice is significantly less than that required to separate water by evaporation, although for the same energy input required, freezing will generally be more expensive than heating [3].

In some applications, freezing can perform a separation with 75-90% reduction of the energy required by convention distillation; acetic acid and acrylic acid refining are two examples [4]. Considering the application of interest, namely, Fischer–Tropsch acid water treatment, freezing appeared to have promise, particularly for application in Canada.

All freeze separation processes are based on the difference in component concentrations between solid and liquid phases that are in equilibrium. This can be understood by referring to Figure 4.l. In this figure Tm_A and Tm_B are melting points of component A and B. When a solution with concentration represented by Point X is cooled, there will be some temperature at which a solid crystalline phase begins to appear in the liquid phase, Point 1. In a binary mixture, a point is eventually reached where both components crystallize simultaneously; this is called the eutectic, and is shown as Point E. At the eutectic, the concentrations of the solid and liquid phase remain constant. At the eutectic point, removal of more heat converts more of the liquid phase to solid but without any change in temperature. The crystals of each component formed are pure. In some cases, it is possible to separate these solid phases by appropriate density segregation or other solid-solid fractionation techniques [4].

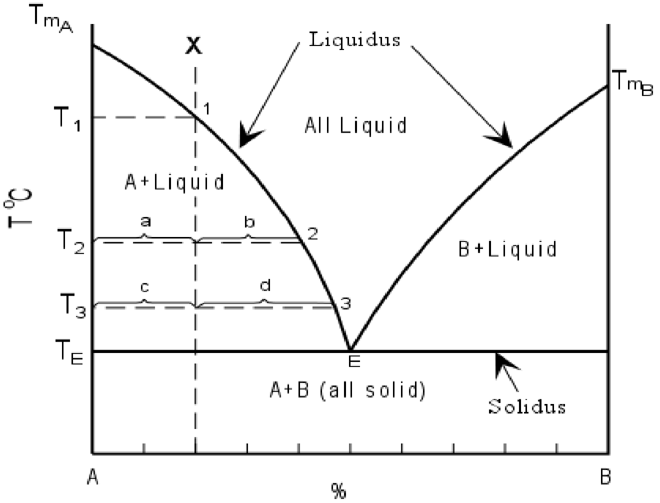

Figure 4.1. Solid-liquid phase equilibrium diagram.

Aqueous product from Fischer Tropsch process also called acid water contains carboxylic acids. The acid enriched effluent stream contains 1 to 1.5% v/v $C_2 - C_4$ organic acids with more than 85% acetic acid [5]. Currently acid water is being treated biologically (aerobic and anaerobic processes) by industries (Chapter 3). In aerobic and anaerobic processes, microorganisms are used to disintegrate the carboxylic acids. In colder regions these processes require additional heating to maintain the water at a temperature at which microorganisms can grow. Heating the feed means increase in the operating cost of these processes.

Fractional freezing can be used as an alternative technique to treat acid water. Fractional freezing reduces the temperature of the solution (carboxylic acid aqueous solution) causing one component (water) to crystallize and thereby concentrate the solution (concentrated carboxylic acid aqueous solution. When fractional freezing is applied in colder regions, for part of the year, the feed solution can be cooled by ambient heat exchange rather than by a chiller-loop. Thus, reducing the cost of cooling.

Solid-liquid equilibrium data for C_2-C_4 carboxylic acid aqueous solution was obtained [6]. Due to the critical importance of this to the design concept, the data was verified by performing experiments. During experiments, temperature of 1wt% of C_2-C_4 carboxylic acid aqueous solution at room temperature was decreased to eutectic point. This was done for each acid separately. This process produced a solid phase (ice crystals) and a concentrated liquid phase, which contained both the components (carboxylic acid and water). From experiments, thermodynamic data for each acid was obtained and compared with literature data. The experimental data matched well with literature. To remove carboxylic acids from concentrated liquid phase, a conceptual design was developed where fractional freezing was followed by distillation. Distillation resulted in removal of carboxylic acids from concentrated solution (liquid phase) which was output of fractional freezing. During distillation carboxylic acids were recovered, rather than being consumed as in the biological processes. Finally a cost evaluation was performed.

2. Experimental

2.1. Materials

Acetic acid (99.7%), propionic acid (≥99.5%) and butyric acid (≥99%) used were purchased from Sigma Aldrich. For titration 1M standard solution of sodium hydroxide supplied by Sigma Aldrich was used. Solutions were prepared in distilled water (conductivity around 3 μS/cm at 25ºC) from Milli-Q (serial no. F1PA 38231B, 0.01 g readability) purchased from Millipore.

2.2. Equipment and procedure

For experiments, 8.00 g of each acid was mixed with distilled water to prepare 800.00 g 1wt% solution of each acid (acetic acid, propionic acid and butyric acid). Weighing of solutions was done using Mettler Toledo MT ML3002E (0.01-3200 g range) balance.

Prepared solutions of 1wt% acetic acid, propionic acid and butyric acid each were placed in separate 1000 ml Erlenmeyer flasks purchased from Fischer Scientific. These 1000 ml flasks were placed in a chiller from Julabo Scientific FP 50-MA (-50 to 200°C range, temperature control accurate to 0.02°C). The chiller was used to decrease the temperature of the solutions from room temperature to their eutectic points. Decrease in temperature was done step wise with intervals of upto 5°C starting from -1°C to the eutectic point temperature of each acid. The eutectic points from literature were -27°C for acetic acid, -29.4°C for propionic acid and -13.4°C for butyric acid [6].

As temperature decreased to 0°C and below, water in the solution started to freeze. More than 24 hours was allowed at each temperature to reach equilibrium. The acid concentration in the liquid was determined by titration (Section 2.3).

At each temperature, after freezing of around 90% water from the solution, the concentrated solution left in the flask was separated from ice crystals and its concentration was determined (also by titration). A new solution of same concentration, as the solution separated from ice crystals, was prepared and placed in chiller for further freezing. This was necessary to improve accuracy of measurements and to avoid inclusion of acid in the ice due to too rapid freezing of the liquid phase of much reduced volume. The process was repeated until the solid-liquid equilibrium was attained at that temperature.

2.3. Analysis

The concentration of the carboxylic acids in carboxylic acid aqueous solution was determined by titrating it against 1 M standard sodium hydroxide with phenolphthalein as indicator. Glass Burette (50 ml burette, 1/10 ml, A grade glass) from Kimax Kimble was employed for performing titration.

2.4. Conceptual design methodology

A conceptual design was developed to achieve higher level of carboxylic acid removal from acid water. In this design, fractional freezing was followed by distillation. So, the liquid phase outlet from the phase separator after the chiller was the feed for the distillation column.

Thermodynamic data for acetic acid, propionic acid and butyric acid in water was obtained from literature [6] and was verified by performing experiments. With the help of thermodynamic data from experiments, material and energy balance was performed taking base of 100 m^3/h of 1wt% of each acid (C_2-C_4 carboxylic acids) in water separately.

Process simulation software was employed to determine the energy and material balance of the distillation column. The process simulation software used was VMGSim for acetic acid and propionic acid and Aspen plus for butyric acid. Thermodynamic models used for acetic acid were NRTL and Hayden O'Connell (HOC), for propionic acid UNIQUAC and HOC and for butyric acid UNIQUAC. The NRTL, UNIQUAC and HOC are popular models for multicomponent vapor-liquid equilibria (VLE) and have been used for carboxylic acid and water [7]. However, the validity of these models was not confirmed. For all the three acids reflux ratio of 5 and pressure of 1 atm was used. Aspen plus was used for butyric acid instead of VMGSim because with VMGSim using thermodynamic models for VLE (NRTL, HOC, UNIQUAC), it did not converge for the given no of trays and reflux ratio.

3. Results and Discussion

3.1. Solid-liquid equilibria data

At a starting composition 1wt% carboxylic acid and at temperature 25°C, nothing happens as the solution is cooled until it reaches temperature 0°C, the initial crystallization temperature. At this point pure water crystals start to form and the composition of the remaining liquid then becomes richer with acid. As heat is removed from the solution more water crystals are formed, but the crystallization temperature also decreases. Eventually the composition is changed sufficiently that the remaining solution achieves the eutectic composition and then acid begins to crystallize.

Amount of solid and liquid at equilibrium was calculated by using following equation:

$$\text{Crystals of A (ice crystals, \%)} = \frac{b}{a+b} \times 100 \qquad \ldots 4.1$$

$$\text{Liquid (water + carboxylic acid, \%)} = \frac{a}{a+b} \times 100 \qquad \ldots 4.2$$

Where,

a = Initial concentration (wt%)
b = Final concentration (wt%)

For a and b, refer to Figure 1.

3.1.1. Acetic acid

Solid-liquid phase equilibrium was obtained by freezing 1wt% acetic acid aqueous solution at different temperatures. The experimentally determined data is presented in Table 4.1. Experiments and analysis at each temperature was done once.

Table 4.1. Decrease in temperature of 1wt% acetic acid aqueous solution to its eutectic point stepwise and equilibrium concentration of acetic acid and percentage of solid and liquid at equilibrium.

T (°C)	Acetic Acid equilibrium conct. (%wt)	Solid (wt%)	Liquid (wt%)
-1.00	2.60	61.5	38.4
-5.00	15.00	93.3	6.7
-10.00	28.00	96.4	3.6
-15.00	39.00	97.4	2.6
-20.00	49.80	98.0	2.0
-25.00	57.04	98.2	1.7
-27.00	58.00	98.3	1.7

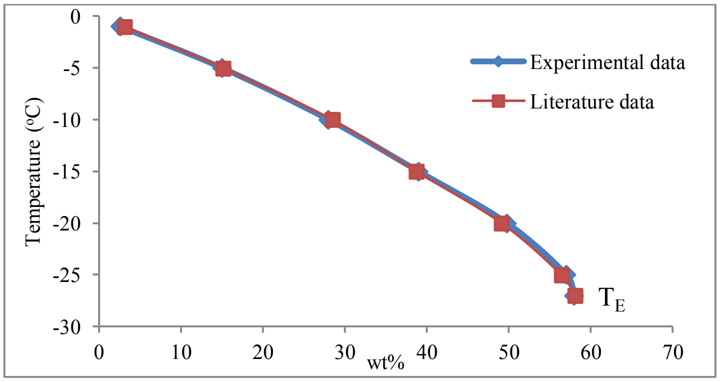

Figure 4.2. Experimental and Literature [6] Solid-liquid equilibrium data starting from 1 wt% of acetic acid in water.

Starting with 1wt% acetic acid aqueous solution and decreasing its temperature stepwise from -1°C to its eutectic point -27°C, solid-liquid equilibrium was attained at concentration of acetic acid in water presented in Table 4.1. Percentage of solid (ice crystals) and liquid (acetic acid and water) at equilibrium was also calculated, shown in Table 4.1.

In Figure 4.2, the point T_E is the eutectic temperature, or composition of acetic acid and is the temperature at which both Components 1 (acetic acid) and 2 (water) crystallize simultaneously. The curve between the eutectic point and the feed (1wt% acetic acid solution) is the solid-liquid equilibria line for various compositions.

From the experimental results of acetic acid it can be said that as temperature of the acetic acid aqueous solution was decreased, the equilibrium concentration of acetic acid in water increased and amount of solids formed (ice crystals) at equilibrium increased as well. Results were compared with literature data and the experimentally determined solid-liquid equilibria matched literature data well, Figure 4.2.

3.1.2. Propionic acid

Solid-liquid equilibrium data for propionic acid was obtained from experiments. Results for propionic acid are presented in Table 4.2. Experiments and analysis at each temperature was done once.

Table 4.2. Decrease in temperature of 1wt% propionic acid aqueous solution to its eutectic point stepwise and equilibrium concentration of propionic acid and percentage of solid and liquid at equilibrium.

T (°C)	Propionic Acid equilibrium conct. (%wt)	Solid (wt%)	Liquid (wt%)
-1.00	4.50	77.77	22.22
-5.00	19.90	94.97	5.03
-10.00	49.62	97.98	2.02
-15.00	66.56	98.49	1.50
-20.00	79.20	98.73	1.26
-25.00	82.92	98.79	1.21
-29.40	87.50	98.85	1.14

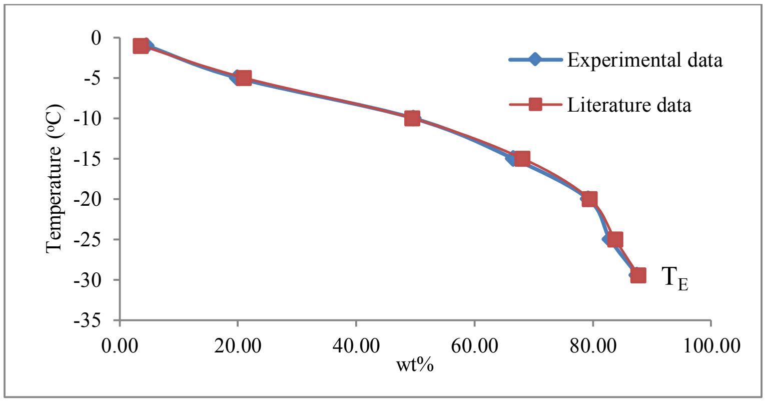

Figure 4.3. Experimental and Literature Solid-liquid equilibrium data starting from 1 wt% of propionic acid in water.

Experiments for 1wt% propionic acid aqueous solution were started form -1°C to its eutectic point -29.4°C and equilibrium propionic acid concentration in water was obtained at each step of temperature. Amount of solid and liquid at equilibrium was calculated. Same trend was observed for propionic acid as acetic acid. With the decrease in temperature, equilibrium concentration of propionic acid in water increased and so did amount of solid (ice crystals). The only difference from acetic acid was that eutectic point temperature of propionic acid (-29.4°C) is lower than acetic acid (-27°C).

Experimental data was compared with literature data. Results are presented in Figure 4.3.

3.1.3. Butyric acid

For 1wt% butyric acid aqueous solution temperature was decreased from -1°C to its eutectic point -13.4°C. Experimental results are presented in Table 4.3. Experiments and analysis at each temperature was done once.

Table 4.3. Decrease in temperature of 1wt% butyric acid aqueous solution to its eutectic point stepwise and equilibrium concentration of butyric acid and percentage of solid and liquid at equilibrium.

T (°C)	**Butyric Acid equilibrium conct. (%wt)**	**Solid (wt%)**	**Liquid (wt%)**
-1.00	4.41	30.56	22.70
-3.02	22.91	95.63	4.37
-4.00	69.60	98.56	1.44
-7.00	79.29	98.74	1.26
-11.00	85.46	98.83	1.17
-13.40	87.22	98.85	1.15

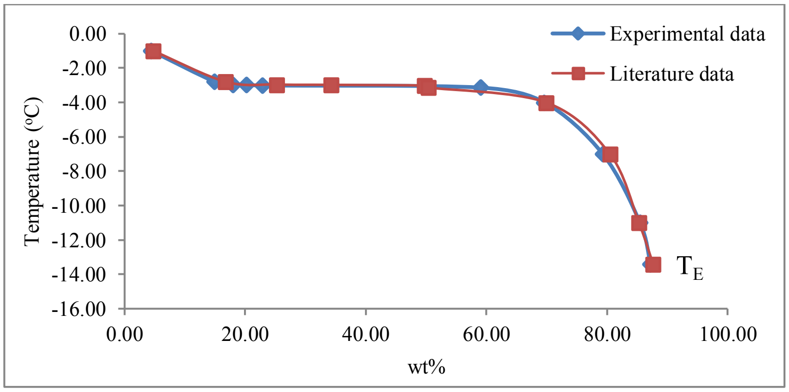

Figure 4.4. Experimental and Literature Solid-liquid equilibrium data starting from 1 wt% of butyric acid in water.

It was observed that for butyric acid solution, over the temperature range of -2.8 to -4.0°C concentration increased from 14.97 to 69.90wt%, which was different from the other two acids where concentration change with temperature was almost consistent. This is because the solubility of the butyric acid in water (around $6x10^4$ mg/L at 25°C) is less than the solubility of acetic acid ($10x10^6$ mg/L) and propionic acid ($1x10^6$ mg/L) in water [8].

3.2.Conceptual design

A conceptual design where fractional freezing of acid water was followed by distillation was developed. This was done to achieve maximum carboxylic acid removal from the 1wt% aqueous carboxylic acid solution. A general process schematic of the separation process is shown in Figure 4.5. The major components of the process include:

a. A Chiller or crystallizer C-101, where a portion of the solution is changed to the solid phase by removing heat.
b. A Separator (Filter) F-101, where the crystal phase is separated from the remaining solution and the crystals are washed to remove adhering solution from the surface.
c. A Distillation column D-101, where separation of water from acid takes place.
d. Heat Exchangers HE-101 and HE-102, to recover the cold energy from the process streams, for cooling the fresh feed material.

The general operating mode is as follows: Feed, 100 m^3/h 1wt% carboxylic acid aqueous solution at 25°C, enters the process through heat exchangers HE-101 followed by HE-102. In heat exchangers the feed temperature was lowered by heat exchange with the cold concentrated solution and product (water) exiting the system. This feed then enters the chiller C-101 where water in solution was converted into crystals until solid-liquid equilibrium was attained. The crystals were pumped as slurry from the chiller to a filter that separated the liquid from the slurry, and the ice crystals were washed with a small portion (10wt%) of melted product. The washed crystals are then melted by contact with feed in heat exchanger HE-102 through a heat exchange surface. Part of the melted product is recycled to wash crystals on the filter. The concentrated acid solution was fed to distillation column D-101 where acid was separated from the water. Water (ice crystals) from the chiller and the overhead product from distillation were combined to produce the water discharged from the process. The concentrated acid solution produced as by-product from cleaning had petrochemical value.

A filter was used to separate ice from concentrated acid solution from chiller instead of hydrocyclone. The reason for not using hydrocyclone was that it is not possible to have both good solids removal and a high underflow concentration in a hydrocyclone. Hydrocyclones are most efficent between 5 to 25% solids. Feed with more than 25% solid decreases classifying sharpness. The underflow concentraion can be upto maximum of 50 vol% for slurries of limestone or coal. There is always some percentage of solids in the overflow as well [12]. As the solid concentration for all the three acids reached more than 50% at some temperature a hydrocylone could not be used.

Modelling of the distillation column was done using process simulation software (see Section 2.4) in order to determine the energy balance and number of trays required for separation of carboxylic acids from water.

Finally cost evaluation of this conceptual design was performed.

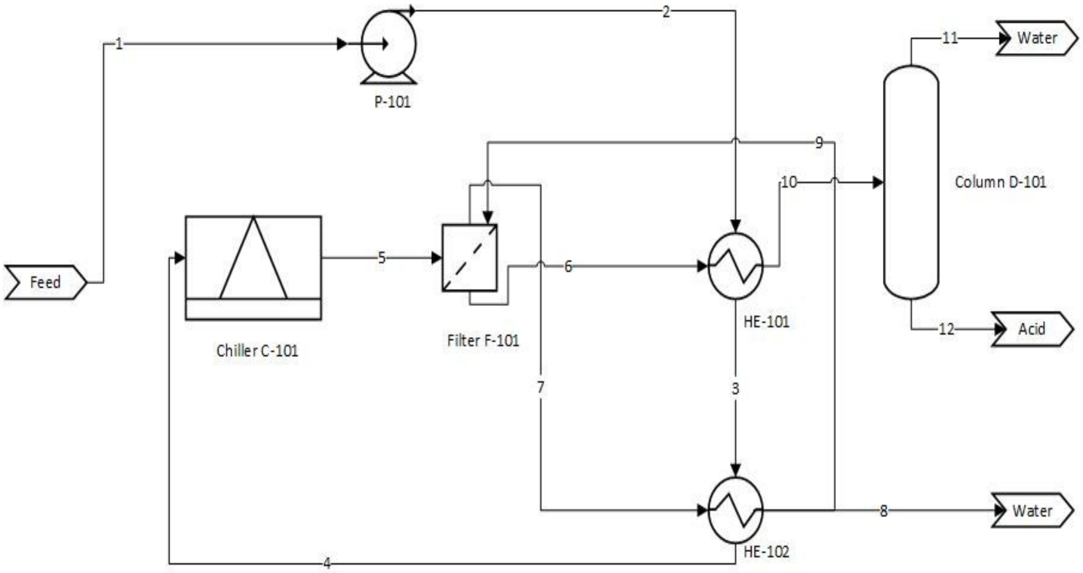

Figure 4.5. Fractional freezing and Distillation process diagram (a conceptual design).

Material balance over conceptual design (Figure 4.5) is presented in Table 4.4.

Table 4.4. Material balance over the conceptual design for feed of 100 m^3/h for acetic acid, propionic acid and butyric acid in water, separate for each acid.

	Acetic acid			Propionic acid			Butyric acid		
Stream	**Flow (t/h)**	**Temperature (°C)**	**wt%**	**Flow (t/h)**	**Temperature (°C)**	**wt%**	**Flow (t/h)**	**Temperature (°C)**	**wt%**
1	100.0	25	1	10.0	25	1	100	25	1
2	100.0	25	1	100.0	25	1	100	25	1
3	100.0	10	1	100.0	10	1	100	10	1
4	100.0	5	1	100.0	5	1	100	5	1
5	100.0	-1	2.6	100.0	-1	4.5	100	-1.0	4.41
		-5	15.0		-5	19.9		-3.0	22.91
		-10	28.0		-10	49.6		-4.0	69.6
		-15	39.0		-15	66.6		-7.0	79.29
		-20	49.8		-20	79.2		-11.0	85.46
		-25	57.0		-25	82.9		-13.4	87.22
		-27	58.0		-29.4	87.5			
6	44.6	-1	2.2	30.0	-1	3.3	72.5	-1.0	4.2
	16.0	-5	6.3	14.5	-5	6.9	13.9	-3.0	7.2
	13.2	-10	7.6	11.8	-10	8.5	11.3	-4.0	8.9
	12.3	-15	8.1	11.4	-15	8.8	11.1	-7.0	9.0
	11.8	-20	8.5	11.1	-20	9.0	11.1	-11.0	9.0
	11.6	-25	8.7	11.1	-25	9.0	11.0	-13.4	9.1
	11.6	-27	8.7	11.0	-29.4	9.1			
7	55.4	-1	0	70.0	-1	0	27.5	-1.0	0
	84.0	-5	0	85.5	-5	0	86.1	-3.0	0
	86.8	-10	0	88.2	-10	0	88.7	-4.0	0
	87.7	-15	0	88.6	-15	0	88.9	-7.0	0
	88.2	-20	0	88.9	-20	0	88.9	-11.0	0
	88.4	-25	0	88.9	-25	0	89.0	-13.4	0
	88.4	-27	0	89.0	-29.4	0			
8	49.8	5	0	63.0	5	0	24.8	5	0
	75.6	5	0	76.9	5	0	77.5	5	0
	78.1	5	0	79.4	5	0	79.8	5	0
	78.9	5	0	79.8	5	0	80.0	5	0
	79.4	5	0	80.0	5	0	80.1	5	0
	79.6	5	0	80.0	5	0	80.1	5	0
	79.6	5	0	80.1	5	0			
9	5.5	5	0	7.0	5	0	2.8	5	0
	8.4	5	0	8.5	5	0	8.6	5	0
	8.7	5	0	8.8	5	0	8.9	5	0

	8.8	5	0	8.9	5	0	8.9	5	0
	8.8	5	0	8.9	5	0	8.9	5	0
	8.8	5	0	8.9	5	0	8.9	5	0
	8.8	5	0	8.9	5	0			
10	44.6	10	2.2	30.0	10	3.3	72.5	10	4.2
	16.0	10	6.3	14.5	10	6.9	13.9	10	7.2
	13.2	10	7.6	11.8	10	8.5	11.3	10	8.9
	12.3	10	8.1	11.4	10	8.8	11.1	10	9.0
	11.8	10	8.5	11.1	10	9.0	11.1	10	9.0
	11.6	10	8.7	11.1	10	9.0	11.0	10	9.1
	11.6	10	8.7	11.0	10	9.1			
11	43.6	100	0.1	29.0	100	0.1	60.8	100	0.1
	15.0	100	0.1	13.5	100	0.1	13.7	100	0.1
	12.2	100	0.1	10.8	100	0.1	10.7	100	0.1
	11.3	100	0.1	10.3	100	0.1	10.6	100	0.1
	10.8	100	0.1	10.1	100	0.1	10.5	100	0.1
	10.5	100	0.1	10.1	100	0.1	10.5	100	0.1
	10.5	100	0.001	10.0	100	0.001			
12	1.0	114	0.94	1.0	123	0.98	11.7	124	0.991
	1.0	114	0.96	1.0	123	0.99	0.2	124	0.999
	1.0	114	0.96	1.0	123	0.99	0.6	124	0.999
	1.0	114	0.96	1.0	123	0.98	0.5	124	0.999
	1.0	114	0.96	1.0	123	0.99	0.5	124	0.999
	1.0	114	0.96	1.0	123	0.98	0.5	124	0.999
	1.0	114	0.96	1.0	123	0.98			

3.3.Energy for freezing

Energy required (Q_1) for freezing of the water in carboxylic acid aqueous solution was calculated in three parts:

a. Energy required to decrease the temperature from 25°C to 0°C (q_1).
b. Energy required to freeze the water at 0°C (q_2).
c. Energy required to decrease the temperature from 0°C to the required temperature (q_3).

As concentration of carboxylic acids in water is low, the binary mixture of carboxylic acid and water was assumed to be pure water for the calculations. Energy required (Q_1) to decrease the temperature of the 1wt% C_2-C_4 carboxylic acid aqueous solutions in the chiller was calculated by using following equations:

$$q_1, q_3 = mC_P dT \qquad \ldots 4.3$$

$$q_2 = m\Delta H \qquad \ldots 4.4$$

$$Q_1 = q_1 + q_2 + q_3 \qquad \ldots 4.5$$

Where,

Q_1 = Amount of energy (W)

m = Mass flow rate (kg/h)

C_P = Specific heat (J/kg.s)

T = Temperature (K)

ΔH = Heat of fusion (J/kg)

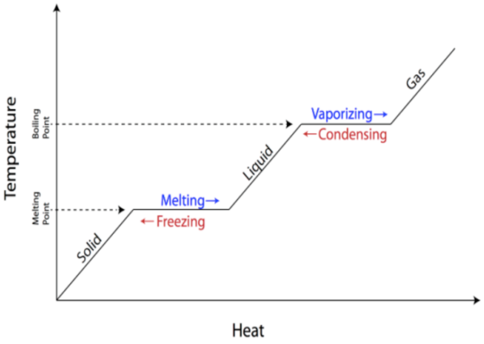

Figure 4.6. Phase transition diagram.

Calculated values for energy (Q_1) are presented in Table 4.5.

Table 4.5. Calculated values of energy required to decrease the temperature of carboxylic acid aqueous solution from 25°C to required freezing temperature.

T_{in} (°C)	T_{out} (°C)	q_1 (MW)	q_2 (MW)	q_3 (MW)	Q_1 (MW)
5	-1	-0.58	-9.28	-0.06	-9.92
5	-5	-0.58	-9.28	-0.29	-10.15
5	-10	-0.58	-9.28	-0.59	-10.44
5	-15	-0.58	-9.28	-0.88	-10.73
5	-20	-0.58	-9.28	-1.17	-11.03

5	-25	-0.58	-9.28	-1.46	-11.32
5	-27	-0.58	-9.28	-1.58	-11.44
Average					**-10.6**

Average energy of 10.6 MW needs to be extracted from the carboxylic acid solution to freeze it and this will be done in chiller.

3.4. Energy for distillation

Simulation software VMGSim and Aspen plus were used for simulation over distilllation column. These simulation softwares provided energy and number of trays required for separation of carboxylic acids and water from concentrated carboxylic acid aqueous solution (chiller outlet). When 1wt% carboxylic acid aqueous solution was fed directly to distillation column without concentrating it in chiller (Q1 = 0) there was no sepataration of caboxylic acid and water.

Each carboxylic acid (C_2-C_4) solution from chiller was as a separate design case, even though these acids would appear as a mixture in an actual Fischer-Tropsch acid water stream. The bottom product concentration of acids achieved was 96wt% acetic acid; 98wt% propionic acid and 99.8wt% butyric acid and overhead product was 99.9wt% water. The results of simulation are presented in Table 4.6, 4.7 and 4.8 for acetic acid, propionic acid and butyric acid, respectively.

Table 4.6. Energy required by distillation column operating at 1 atm pressure to separate acetic acid (overhead 96 wt%) and water (bottom 99.9 wt%) using VMGSim with thermodynamic models NRTL and Hayden O'Connell and reflux ratio of 5.

T (^{o}C)	Condenser (MW)	Reboiler Q_2 (MW)	No. of Trays
-1.00	163.5	168.0	20
-5.00	56.1	57.8	20
-10.00	45.7	47.0	20
-15.00	42.3	43.5	20
-20.00	40.4	41.6	20
-25.00	39.6	40.7	20
-27.00	39.5	40.6	20

Table 4.7. Energy required by distillation column operating at 1 atm pressure to separate propionic acid (overhead 98 wt%) and water (bottom 99.9 wt%) using VMGSim with thermodynamic models UNIQUAC and Hayden O'Connell and reflux ratio of 5.

T (ºC)	Condenser (MW)	Reboiler, Q_2 (MW)	No. of Trays
-1.00	108.8	111.8	22
-5.00	50.7	52.2	22
-10.00	40.6	41.7	22
-15.00	38.8	39.9	22
-20.00	40.4	41.6	22
-25.00	37.8	38.9	22
-29.40	37.6	38.7	22

Table 4.8. Energy required by distillation column operating at 1 atm pressure to separate butyric acid (overhead 98 wt%) and water (bottom 99.9 wt%) using Aspen plus with thermodynamic models UNIQUAC and reflux ratio of 5.

T (ºC)	Condenser (MW)	Reboiler, Q_2 (MW)	No. of Trays
-1.00	225.37	232.40	20
-3.02	48.61	50.05	20
-4.00	39.115	39.11	20
-7.00	38.521	40.28	20
-11.00	38.217	39.68	20
-13.40	38.138	39.36	20

3.5. Fractional freezing and distillation

Energy required to freeze the water in carboxylic acid aqueous solution (Q_1) and energy required for the sepatation of the carboxylic acids and water in the distillation column (Q_2) were plotted against total energy required required for separation of carboxylic acids from water ($Q_1 + Q_2$). The plots are presented in the Figure 4.6 and 4.7.

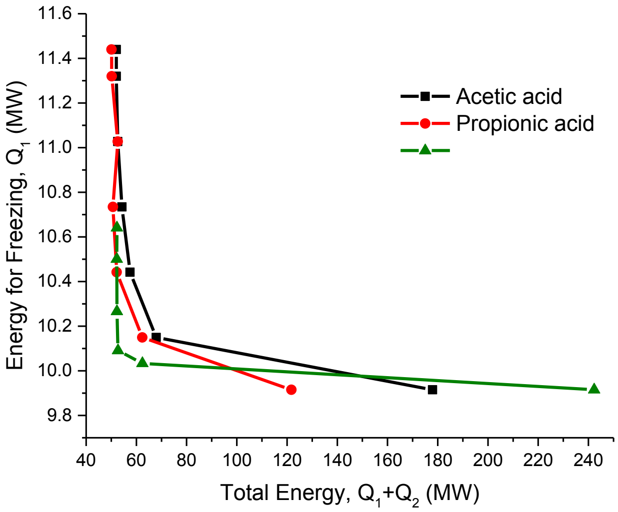

Figure 4.7. Energy for freezing vs total energy required for sepatation for acetic acid, propionic acid and butyric acid.

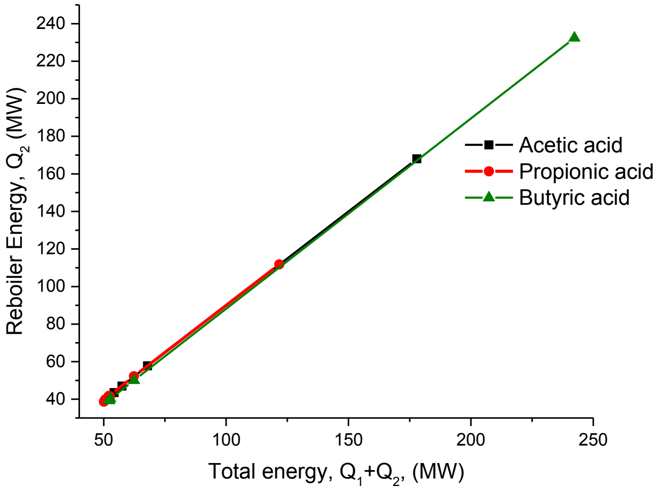

Figure 4.8. Energy for distillation vs total energy required for sepatation for acetic acid, propionic acid and butyric acid.

When temperature of the carboxylic acid solution was decreased more energy was required to freeze the water in the solution. As can be seen from Figure 4.6, as temperature of carboxylic acid aqueous solution was decreased to the eutectic point of each acid, more energy for freezing (Q_1) was used. However, as temperature decreased solid-liquid equilibrium was attained at higher acid concentration giving more percentage of solids. The concentration of water in the solution at equilibrium was already less. Therefore, less energy was required to separate acid and water in distillation column which is evident from Figure 4.7.

For T = -1°C less energy was required by chiller to reduce the temperature of carboxylic acid solution to this temperature but for distillation a lot more more energy was required than for rest of the temperautes. It could be because benefits from distillation becomes less at less carboxylic acid concentration in water. For T = -1°C concentration of acids at equilibrium is quite low which means the solution that is fed to distillation has low concentration of acids and therefore more enrergy will be required to separate the carboxylic acid and water. This can be related to when simulation of 1wt% carboxylic acid aqueous solution was done over distillatin column (was fed directly to distillation column without passing through chiller first) and because of low concentration of carboxylic acid in water there was no separation.

From Figure 6, the optimum temperture at which chiller should be operated for acetic acid, propionic acid and butyric acid is -5°C. As for all the three acids at this temperature there is dip in the curves. Freezing energy (Q_1) at this temperature is minimum. However, optimum temperatures for distialltion was eutectic points of each acid that is -27, -29.4 and -13.4°C.

3.6. Cost evaluation

Cost evaluation was done by calculating capital cost and operational cost of each equipment used in the conceptual design, which are chiller, heat exchangers and distillation column. The general assumptions for the cost estimation are outlined in Chapter 3.

3.6.1. Capital cost

a. Chiller

Capital cost of chiller was calculated by calculating heat exchange area. Following equations were used to calculate area of chiller:

$$Q' = (mC_P dT)_{Liq} + m\Delta H + (mC_P dT)_{solid} \qquad \ldots 4.6$$

$$Q'' = UA\Delta T \qquad \ldots 4.7$$

$$Q' = Q'' = Q \qquad \ldots 4.8$$

Where,

Q = Amount of energy (W)

Q' = Amount of energy extracted from carboxylic acid solution to freeze water in it (W)

Q'' = Amount of energy transferred in heat exchanger (W)

m = Mass flow rate (kg/h)

C_P = Specific heat (J/kg.s)

U = Overall heat transfer coefficient (J/m^2.s.K)

A = Heat transfer area (m^2)

T = Temperature (K)

For capital cost of chiller, average area of chiller for propionic acid was considered, as its eutectic point is highest (on negative side of temperature) of three acids. Average of 106 m^2 for all the three acids was used for further calculations. Results are presented in Table 4.9.

Table 4.9. Cost evaluation of chiller operating from -1 to -27°C at atmospheric pressure with feed at temperature of 5°C. Currency in US dollars, year 2013.

Tout (°C)	**Tin (°C)**	**Q_2 (MW)**	**A (m^2)**
-1.00	5.00	9.9	1941
-5.00	5.00	10.1	1188
-10.00	5.00	10.4	815
-15.00	5.00	10.7	629
-20.00	5.00	11.0	517
-25.00	5.00	11.3	443
-27.00	5.00	11.4	419
Average			850

b. Distillation column

Equations used to evaluate the capital cost of distillation:

$$U_{sg} = K_{sb}\left(\frac{\rho_l - \rho_g}{\rho_g}\right)^{0.5} \qquad \ldots 4.9$$

$$D = \left(\frac{4 \times V \times M}{(\pi \times \rho_g \times U_{sg})}\right)^{0.5} \qquad \ldots 4.10$$

$$H_t = 0.5 \times D^{0.3} \qquad \ldots 4.11$$

$$H = \frac{N_t \times H_t}{Murphy\ efficiency} \qquad \ldots 4.12$$

Where,

U_{sg} = Maximum gas velocity in distillation column (m/s)

K_{sb} = Souders-Brown constant (0.09 m/s)

ρ_l = Liquid density in distillation column (kg/m^3)

ρ_g = Gas density in distillation column (kg/m^3)

D = Diameter of distillation column (m)

V = Gaseous molar flow rate (mol/s)

H_t = Tray spacing (m)

H = Height of column (m)

N_t = Number of theoretical stages

$Murphy\ efficiency$ = 0.6

To calculate capital cost of distillation column, its diameter and height were required which were calculated from maximum gas velocity, liquid and gas densities in the distillation column. Maximum gas velocity, liquid and gas densities were obtained from simulation over distillation column using simulation software. Values from simulation and results of calculations are presented in Table 4.10.

Table 4.10. Values of maximum gas velocity, liquid and gas density obtained from VMGSim using NRTL and Hayden O'Connell at atmospheric pressure with reflux ratio of 5. Diameter and height of column calculated for maximum gas velocity, liquid and gas density. Currency in US dollars, year 2013.

T (°C)	Usg (m/s)	D (m)	H_t (m)	H (m)	ρl (kg/m^3)	ρg (kg/m^3)
-1.00	1.9	10.7	1.0	33.9	958.3	2.1
-5.00	1.9	6.6	0.9	29.3	958.3	2.1
-10.00	1.9	5.9	0.9	28.4	958.3	2.1
-15.00	1.9	5.7	0.8	28.1	958.3	2.1
-20.00	1.9	5.6	0.8	27.9	958.3	2.1
-25.00	1.9	5.5	0.8	27.8	958.3	2.1
-27.00	1.9	5.7	0.8	28.2	958.3	2.1

Taking average diameter of column and height, cost of the distillation column was calculated.

c. Heat exchangers

Area of heat exchangers HE-101 and HE-102 was calculated using process simulation software Aspen plus. Thermodynamic model used was NRTL. Feed (1 wt% carboxylic acid aqueous solution) at 25°C was feed to HE-101 to cool it down to 10°C by exchanging heat to chiller outlet (concentrated carboxylic acid aqueous solution from fractional freezing), as shown in Figure 4.11.

Table 4.11. Cost evaluation of HE-101 using Aspen plus with thermodynamic model NRTL. Heat exchanger operating at atmospheric pressure. Currency in US dollars, year 2013.

$Tcold_{in}$ (°C)	$Tcold_{out}$ (°C)	Amount of Energy exchanged, Q (MW)	U (W/m^2.K)	A (m^2)
-1.00	10	0.54	850	35.7
-5.00	10	0.26	850	14.7
-10.00	10	0.28	850	14.7
-15.00	10	0.33	850	15.8
-20.00	10	0.38	850	16.9
-25.00	10	0.43	850	18.2
-27.00	10	0.40	850	16.6
Average				**18.9**

Outlet of HE-101 at 10°C was fed to HE-102 to further cool down the feed. In HE-102 heat exchange occurred with solid phase (ice crystals) of fractional freezing. Aspen plus with thermodynamic model NRTL was used to calculate heat exchange area.

Table 4.12. Cost evaluation of HE-102 using Aspen plus with thermodynamic model NRTL. Heat exchanger operating at atmospheric pressure. Currency in US dollars, year 2013.

$Tcold_{in}$ (°C)	**$Tcold_{out}$ (°C)**	**Amount of Energy exchanged, Q (MW)**	**U ($W/m^2.K$)**	**A (m^2)**
-1.00	5	0.37	850	70.4
-5.00	5	0.94	850	192.4
-10.00	5	1.46	850	289.4
-15.00	5	1.97	850	376.3
-20.00	5	2.48	850	457.2
-25.00	5	2.98	850	531.3
-27.00	5	3.18	850	565.8
Average				**354.7**

Table 4.13. Capital cost summary of conceptual design for Fractional freezing of 1wt% acetic acid aqueous solution operating at 1 atm pressure. Lang factor 3 and cost index for year 2004 and 2013 used 400 and 480, respectively. Plant location Canada, currency in US dollars for the year 2013.

Equipment Identification	**Number**	**Capacity or size specifications**	**Purchased equipment cost (base material)**		**Material factor, F_M**	**Pressured or other factors, F_P**	**Actual bare module factor, F^a_{BM}**	**Actual bare module cost, C^a_{BM}**	**Total (million $)**
			Year 2004	Target year, 2013					
Chiller	C-101	850 m^2, Stainless Steel, 1 atm	1.5x10^5	1.8x10^5	2.3	1	3.5	0.6.	1.890
Distillation Column	D-101	5 m ID * 30 m vertical, Stainless Steel, 1 atm	1x10^5	1.2x10^5	1	1.2	3.4	0.408	1.224
Tray		4 m ID, Stainless Steel	5.2x10^3	6.3x10^3	-	-	2.2	0.277	0.041
Heat Exchanger	HE-101	18.9 m^2, Stainless Steel, 1 atm	6 x10^3	7.2 x10^3	1	2.3	2	0.0144	0.043
Heat Exchanger	HE-102	354.7 m^2, Stainless Steel, 1 atm	2.5 x10^4	3 x10^4	1	2.3	2	0.060	0.18
Heat Exchanger		134 m^2, Stainless Steel, 1 atm	2 x10^4	2.4 x10^4	1.7	1.2	6	0.14	0.42
Total bare module cost (million $)							C_{TBM}		3.798
Total module cost (million $)							$C_{TM} = C_{TBM}$x1.18		4.482
Auxiliary facility (million $)							C_A=C_{TM}x0.30		1.344
Grass roots capital (million $)							$C_{GR} = C_{TM} + C_A$		5.143
Total capital cost over 20 years plant life with stream factor of 95% ($/m^3)[a]									**0.309**

[a] The capital cost was converted to an operating cost per m^3 feed processed, assuming a discount rate of 0%.

Average area of heat exchangers for acetic acid was used for further calculations, as area calculated for propionic acid and butyric acid were almost same as for acetic acid (propionic acid = 16.1 m^2, butyric acid = 17.8 m^2).

3.6.2. Operational cost

Operating cost of chiller was calculated on the basis of average energy required (Q_1) and operating cost of distillation by average energy for separation of carboxylic acids from water. For distillation cost was calculated from reboiler energy (Q_2).

For chiller, energy was provided by electricity and for distillation heating in reboiler was done with steam.

Table 4.14. Operating cost calculated from energy required for fractional freezing and average energy required for distillation taking cost of electricity generated from natural gas US$5/GJ. Plant location Canada, currency in US dollars and year of 2013.

Operating cost	**MW**	**$/m^3**
Chiller	10.6	1.908
Distillation acetic acid	62.7	4.654
Distillation propionic acid	52.1	3.868
Distillation butyric acid	71.3	5.293

3.6.3. Total treatment cost

Total treatment cost was calculated by adding capital cost of each equipment and total operating cost.

Table 4.15. Total treatment cost calculated for feed of 100 m^3/h of 1wt% carboxylic acid aqueous solution from capital and operating cost for plant location Canada in US dollars for the year 2013.

	Capital Cost	**Average Operating Cost**	**Total Treatment Cost ($/m^3)**
Treatment Cost ($/m^3)	0.309	6.513	6.822

3.6.4. Recovery of carboxylic acids

Acids obtained as overhead product of distillation have market value. Selling these acids would be profitable. Market value of C_2-C_4 carboxylic acids (99.9wt% pure) was determined for the year 2010 [13]. Acids obtained from the conceptual design are not pure (99.9wt %). Therefore discounted price (50%) of the recovered carboxylic acids are presented. Price of carboxylic acids (99.9wt %) in 2013 was assumed same as was in year 2010. From the market price of carboxylic acids, price of the acids recovered from distillation were evaluated, which are presented in the Table 4.13.

Table 4.16. Average cost of carboxylic acids recovered from feed of 100 m^3/h of 1wt% carboxylic acid aqueous solution from the fractional freezing and distillation conceptual design. Plant location Canada, currency in US dollars for the year 2013.

	Market value of Acid (\$/kg)	**Avg. Cost of Acid recovered (\$/m^3)**
Acetic Acid	1.56	8.00
Propionic Acid	2.14	10.79
Butyric Acid	1.15	3.46

4. Conclusions

Fractional freezing was investigated to remove the short chain carboxylic acids (C_2-C_4) from the aqueous product of Fischer Tropsch process. Fractional freezing along with distillation was studied, whether it can be used as an alternative technique for removal of acids, which included removal of acids and the technique being economical so that it can be used instead of conventional methods used in industries. From this work, it can be concluded:

a. During fractional freezing there was increase in concentration of C_2-C_4 carboxylic acids in water and at the same time pure water was obtained as ice crystals.
b. As temperature was decreased percentage of solids (ice crystals) increased.

c. More energy was required to decrease the temperature of the carboxylic acid aqueous solution but as temperature decreased less energy was required in distillation for separation of acids from water.
d. Bottom product achieved from distillation was 96wt% acetic acid, 98wt% propionic acid and 99.8wt% butyric acid and overhead product was 99.9wt% water.
e. The optimum temperature for chiller to operate was -5ºC (chiller temperature) and for distillation was eutectic point of each acid that is -27, -29.4 and -13.4 ºC.
f. Cost evaluation showed that for the conceptual design developed, it takes around \$6.8 to treat 1 m^3 of acid water.
g. Recovered acids from distillation have market value and could be sold, which not only would cover treatment cost but will also give profit in case of acetic acid and propionic acid.

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Chapter 5: Electrolysis

1. Introduction

The anodic oxidation of carboxylic acids commonly denoted as the Kolbe electro-synthesis, is probably one of the most well-known and used electrolytic synthesis method [1]. The Kolbe electro synthesis is not actually an oxidation of the carboxylic acid itself, but rather of its ion. The reaction can be written as:

$$RCOO^{-} \rightarrow RCOO^{\cdot} + e^{-} \qquad \ldots 5.1$$

$$RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2 \qquad \ldots 5.2$$

An electron is discharged from carboxylate ion and is transferred to the anode followed by decarboxylation giving radical ($R^{\cdot}$) as first intermediate product, shown in equation 5.1 and 5.2. The radical $R^{\cdot}$ undergoes coupling, disproportionation or other reactions giving final products, such as free radical dimerization to give R-R [1]. The $R^{\cdot}$ could also be further oxidized to a carbonium ion at the anode [2], as presented in equation 5.3.

$$R^{\cdot} \rightarrow R^{+} + e^{-} \qquad \ldots 5.3$$

The need for an alternative technique for treatment of Fischer-Tropsch acid water has been outlined in before [3] and this type of electro-synthesis was consequently of interest.

Kolbe electro-synthesis was employed to determine whether it can be used to treat Fischer-Tropsch acid water. Electrolysis of 1wt% acetic acid aqueous solution was done to determine the effect on concentration of acetic acid in water. Experiments were carried out at different temperatures so as to find the effect of temperature on oxidation of acetic acid as well as well as determine operating parameters important for conceptual design and costing.

2. Experimental

2.1.Materials

Acetic acid (99.7%) used was purchased from Sigma Aldrich. For titration 1M standard solution of sodium hydroxide supplied by Sigma Aldrich was used. Solutions were prepared in distilled water (conductivity around 3 μS/cm at 25°C) from Milli-Q (serial no. F1PA 38231B) purchased from Millipore. Nitrogen (99.999 %) from Praxair was employed for providing an inert atmosphere.

2.2.Equipment and procedure

500 g of 1wt% acetic acid in water was prepared by adding 5.00 g of acetic acid in 495.00 g of distilled water. The solution was weighed by using Mettler Toledo MT ML3002E (0.01-3200 g range, 0.01 g readability). Prepared solution of 1wt% acetic acid aqueous solution was placed in a 500 ml glass three arm round bottom flask from Fischer Scientific. A fourth arm (0.8 cm dia.) was added to glass flask to fit the electrode. A DC power supply from Keysight Technologies (U8032A, triple outlet, 60V/3A, accuracy for constant voltage ≤0.25% + 15 mV, accuracy for constant current ≤0.30% + 15 mA) was employed to provide DC power to the electrolysis system. A carbon electrode (0.7 cm dia., 11.6 cm length) was supplied by Fischer Scientific. The carbon electrode (anode) was used as the working electrode. A lead electrode (0.5 cm dia., 20.5 cm length,

99.99%) was supplied from Alfa Aesar. The lead electrode (cathode) was used as counter electrode. A glass body calomel reference electrode from Fischer Scientific was used as reference electrode so as to keep potential at working electrode constant. A potential was applied to the working electrode (WE) with respect to the reference electrode (RE). As reference electrode has a fixed potential, the potential at the working electrode was monitored and controlled by using reference electrode. The whole setup of electrolysis is shown in Figure 5.1.

The general operation is as follows: Nitrogen gas from cylinder was continuously fed to the electrolysis setup to provide an inert environment. A very low constant nitrogen flow rate was maintained using variable area flowmeter (calibration of which was unavailable). The test cords from Digi-Key (501-1490-ND and 501-1412-ND, 5A) were used to complete the electric circuit from DC power supply.

The Kolbe electro-synthesis is a high potential difference method. Experiments were carried out at constant voltage of 29 V (twenty-nine volts) at four different temperatures, which were 10, 20, 25 and 30^{o}C. For each temperature, experiments were performed for 2 hours and change in current was determined. To see the effect of electrolysis on concentration of acetic acid over longer time, experiments were performed for 8 hours at each temperature (10, 20, 25 and 30^{o}C) and change is current was monitored. To keep the temperature of the electrolysis constant, electrolytic cell was placed in fluid bath of a chiller, Julabo F25-ED chiller (temperature control to $\pm$0.03^{o}C). During the experiment, gaseous product was analyzed continuously. A mass spectrometer (MS) from Extorr (model PM Z01 300) was connected by a T-piece in the off-gas line. The off-gas also passed through an O_2/CO_2 analyzer from Alpha Omega Instruments (Series 9600, 0-5000 ppm CO_2). After the experiments, the liquid was analyzed to determine the concentration of acetic acid in it. During the experiments the change in current was measured and recorded. The current increased with time and for calculations average of the current was employed.

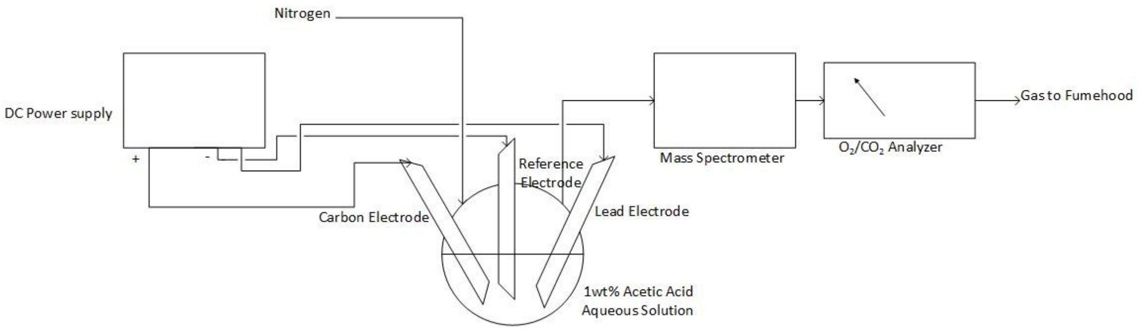

Figure 5.1. Process diagram of electrolysis.

2.3. Analysis

The concentration of the acetic acid in product liquid was determined by titrating it against 1 M standard solution of sodium hydroxide with phenolphthalein as indicator. A glass Burette (2 ml burette, 1/100 ml) from Fischer Scientific was employed for performing the titration.

The gaseous product was checked for the presence of different components like, ethane, methane and CO_2 by using the MS from Extorr (model PM Z01 300). The bulk of the gas was N_2.

An O_2/CO_2 analyzer (Alpha Omega Instruments, Series 9600, 0-5000 ppm CO_2) was employed to detect the presence of CO_2 in gaseous stream.

3. Results and discussion

3.1.Liquid product

Electrolysis of 1wt% acetic acid was carried out at four different temperatures. For each temperature, concentration of acetic acid in the liquid product was determined at end of the experiment. Experimental results are presented in Table 5.1 and 5.2.

Table 5.1. Experimental results of electrolysis of 1wt% acetic acid aqueous solution at different temperatures over 2 hours, experiments being performed in triplicates.

Time (h)	Temp (^oC)	Voltage (V)	Initial Conct. (%wt)	Current (A)		Final Conct. (%wt)	
				x	y	x	y
2	10	29.00	1.005	0.16	0	1.005	0
2	20	29.00	1.005	0.39	0.05	1.000	0.008
2	25	29.00	1.005	0.53	0.09	0.996	0.008
2	30	29.00	1.005	0.54	0.02	0.980	0.009

x = average value

y = standard deviation

Table 5.2. Experimental results of electrolysis of 1wt% acetic acid aqueous solution at different temperatures over 8 hours, experiments being performed once at each temperature.

Time (h)	Temp (^oC)	Voltage (V)	Current (A)	Initial Conct. (%wt)	Final Conct. (%wt)
			x		
8	10	29.00	1.14	1.005	0.975
8	20	29.00	1.26	1.005	0.9157
8	25	29.00	1.39	1.005	0.9007
8	30	29.00	1.41	1.005	0.8857

From Table 5.1 and 5.2, it can be seen that temperature affects the rate of electro-synthesis. The final concentration of acetic acid in water after electrolysis at different temperatures was different. It was observed that over the same length of experimental time, temperature affected oxidation of acetic acid in the feed solution. As temperature was increased, oxidation of acetic acid increased.

At higher temperatures (>50°C), the Kolbe reaction begins to be suppressed [4]. As per literature, with the increase in temperature there should be decrease in the formation of ethane but formation of other products is not affected, for example methane as per disproportionation (Eq. 5.4). It has been reported that an increase in temperature tends to decrease the yield of coupling product but it is not known whether this decrease is accompanied by an increase in the yield of products formed through carbonium ion path [1].

$$R^{\cdot} \rightarrow RH + RH - H_2 \qquad \ldots 5.4$$

From the gaseous product analysis, apart from ethane there was presence of methane as well. This could be the reason that there is still decrease in concentration of acetic acid in water with the increase in temperature.

3.2.Gaseous products

The product gaseous stream was analyzed continuously by passing gases through Mass Spectrometer (MS). From the MS results, it was concluded that there was presence of hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4) and ethane (C_2H_6) in the product gaseous stream [5]. The presence of ethane was because of coupling reaction and presence of methane could be because of disproportionation or because of formation of carbonium.

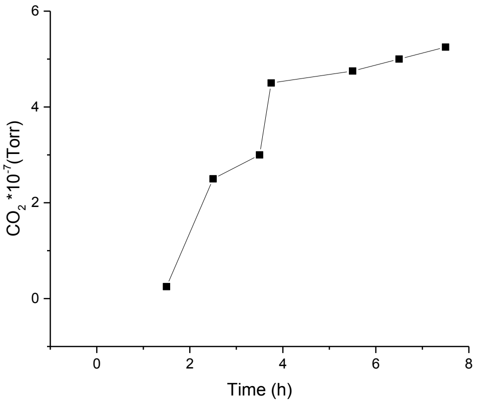

Figure 5.2. Plot of CO_2 against time from MS results with constant nitrogen flow.

It was reported that the volume of CO_2 formed during the anodic oxidation of acetic acid was more than expected form equation. As per Kolbe, the CO_2 obtained was almost double the volume of ethane formed [6]. From the MS results it was observed that as compared to methane and ethane which remained almost constant over time, CO_2 increased with the time (Figure 5.2). Ratio of $CH_4:CO_2$ decreased from 4 to 0.095 and $C_2H_6:CO_2$ decreased from 1 to 0.095 (Figure 5.3). This indicates apart from oxidation of acetate, carboxylic acid group in it was removed as well. The carboxylic acid group of acetic acid removed produces CO_2, which during experiment increased with the time.

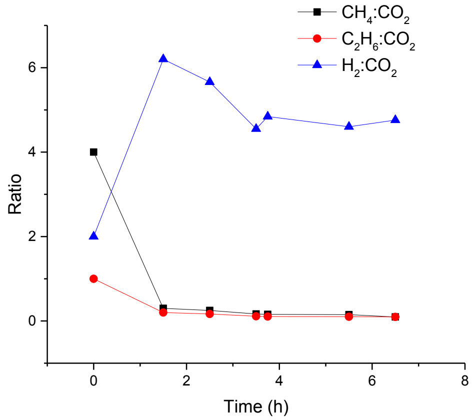

Figure 5.3. Plot of ratio between $CH_4:CO_2$, $C_2H_6:CO_2$ and $H_2:CO_2$ from MS results with constant nitrogen flow.

During experiments H_2 increased with respect to CO_2 as is seen in Figure 5.3. Ratio of $H_2:CO_2$ increased from 2 to 4.76. It has been reported that there is formation of hydrogen at cathode during anodic oxidation of acetate as per Eq. 5.7 [4].

$$2CH_3COOH \rightarrow 2CH_3COO^- + 2H^+ \qquad \ldots 5.5$$

$$2CH_3COO^- \rightarrow 2CO_2 + C_2H_6 + 2e \qquad \ldots 5.6$$

$$2H^+ + 2e \rightarrow H_2 \qquad \ldots 5.7$$

On oxidation of acetate, there should be small amount of oxygen in the products [1]. From the MS results, there was no oxygen present in the gaseous product. It could likely be because in slightly acidic solutions, on electrolysis some oxygen never appears as gas because it is employed to oxidize some acid to carbon dioxide and water [6]. Because of the low concentration of acid and only some of the acid being oxidized with oxygen, the mass of liquid product (mainly water) remained almost same.

Gaseous product stream was passed through CO_2 analyzer to detect the CO_2 in product stream. The CO_2 concentration was around 4900 ppm in the product stream (for reference, the concentration of CO_2 in the atmosphere is around 300 ppm).

3.3.Anode material

For electrolysis in aqueous solutions the nature of the anode is of great importance. Coupling occurs to an appreciable extent only with a smooth platinum (or iridium) anode. The anode used for the experiments was carbon. For carbon electrodes formation of carbonium ions were reported to be predominant reaction [1]. The carbonium ion may react with $RCOO^-$ leading to the formation of ethane as follows [4]:

$$RCOO^- + R^+ \rightarrow R - R + CO_2 \qquad \ldots 5.8$$

These mechanisms have been reported only in those cases where the Kolbe coupling through formation of radical usually fails.

3.4.Voltage

One of the important characteristics of anodic oxidation of carboxylate ion oxidation is that it takes place at high potential. In the low potential region (below 21 V), oxygen evolution due to the oxidation of water takes place. Anodic oxidation of acetate ion starts to occur at about 23 V. This is the critical potential for acetate oxidation, leading to the formation of ethane and CO_2. This was the reason for using 29 V for the experiments. The Kolbe reaction in aqueous solutions usually proceeds with increasing efficiency as the anode potential is raised [4].

3.5.Electrolytic work

As current density for electrolysis is raised, hydrocarbon formation rate increases rapidly. Hydrocarbon becomes the predominant anodic product along with CO_2. After a point the production of hydrocarbon is less with increasing current density. This point of change in hydrocarbon production from high percentage to low is called critical current density. For aqueous acetate solution employing DC at smooth platinum electrodes, critical current density is 0.25 A/cm^2, or 2500A/m^2 [7].

In our work (Table 5.3), voltage was kept constant and current increased with the time. Over same length of experiments, current density increased as temperature of solution was increased and so did the conversion of acetic acid. An increase in current density resulted in increased oxidation of acetic acid but the conversion of acetic acid into ethane was slow. Since critical current density of acetic acid over carbon electrode is not known, so it cannot be concluded that whether the experiments were performed above or below critical current density.

Table 5.3. Calculated current density (A/m^2) for electrolysis of 1wt% acetic acid aqueous solution at 29 V at different temperatures.

Time (h)	Temp (^{o}C)	Voltage (V)	Current (A)	Power (MW/m^3)	Current density (A/m^2)
8	10	29.00	1.14	0.07	336.6
8	20	29.00	1.26	0.07	372.0
8	25	29.00	1.385	0.08	408.9
8	30	29.00	1.405	0.08	526.2

3.6.Cost evaluation

For cost evaluation, assumptions have been outlined in Chapter 3. The feed basis was 100 m^3/h of 1wt% acetic acid aqueous solution at 25^{o}C. To meet outflow requirement, a conversion of 98.0% was needed.

It was assumed that it took 8 hours of electrolysis for acetic acid to reach from initial concentration of 1wt% acetic acid in feed to 200 mg/L in product to reach the conversion of 98.0%. Rate constant for the electrolysis was calculated using equation 5.9. An average rate constant was calculated by integrating the change in concentration over time. The value of rate constant calculated was 1.35x10^{-4}s^{-1}. This procedure was adopted to calculate rate constant to simplify the calculations. The reaction being first order [4], total area of electrode was calculated using Eq. 5.10.

$$-r_A = -\frac{dC_A}{dt} = kC_A \qquad \ldots 5.9$$

$$V' = F_{AO}\int_0^{X_A}\frac{dX_A}{-r_A} = F_{AO}\int_0^{X_A}\frac{dX_A}{kC_A'} = \frac{F_{AO}}{kC_{AO}'}\int_0^{X_A}\frac{dX_A}{(1-X_A)} \qquad \ldots 5.10$$

Where,

C_A = Concentration (mol/L)
t = Time (h)
V' = Area (m^2)
F_{AO} = Molar flow rate (mol/h)
C_{AO}' = Initial moles per unit area (mol/m^2)
X_A = Conversion
$-r_A$ = Rate of reaction ($mol/m^2.h$)

The calculated anode area for the current density of 409 A/m^2 at 25°C was 5435m^2.

The capital cost was calculated using following equation [8]:

$$\text{Installed cost} = £\ 8000\ S^{0.9} \qquad \ldots 5.11$$

Where, S = anode area in m^2. After applying the average conversion rate for year 2013, Eq. 5.11 becomes:

$$\text{Installed cost} = \text{US\$}\ 12467\ S^{0.9} \qquad \ldots 5.12$$

The total capital cost calculated for feed of 100 m^3/h over 20 years in US dollars for the year 2013 was \$ 2.176/m^3, taking cost index for 1995 and 2013 as 380 and 480, respectively [9].

For the operating cost current density of 409 A/m^2 at 25°C, as was observed during experiments, was employed. Table 5.4 presents the results for operating cost. The total operating for treating 100 m^3/h of 1wt% acetic acid aqueous solution to final concentration of 200 mg/L of acetic acid in water was \$11.604/m^3.

As per the experiments performed in lab and products formed, the electrolysis of acetic acid follows the equation 5.13. Heat of reaction was calculated for the Eq. 5.13 and it was endothermic (ΔH=24.6kJ). However, the power required for the electrolysis is quite high. The power for electrolysis (64.5 MW) is much higher than the heat that will be absorbed (24.6kJ or 0.854W) by the solution. Therefore, during winters there is not any need for heating the solution to compensate for ambient heat loss. The operation was considered isothermal as a simplifying conservative assumption.

$$3C_2H_4O_2 \rightarrow CH_4 + C_2H_6 + H_2 + 3CO_2 \qquad \ldots 5.13$$

Table 5.4. Power calculated for 100 m^3/h of 1wt% acetic acid aqueous solution at 29 V and current density of 409 A/m^2 to a conversion of 98.0%.

Area (m^2)	5435
Current density (A/m^2)	409
Current (A)	2.2×10^6
Power (MW)	64.5
Operating cost (\$/m^3)	11.604

Therefore, total cost of treating 1wt% acetic acid aqueous solution at the feed rate of 100 m^3/h for the year 2013 is \$13.780/m^3.

4. Conclusion

Electrolysis was studied as one of the techniques for treatment of Fischer-Tropsch acid water. Electrolysis of 1wt% acetic acid in water was carried out at a constant voltage of 29 V and at different temperatures, which were 10, 20, 25 and 30°C. From this work it can be concluded that:

a. There was decrease in concentration of acetic acid by employing electrolysis. At constant voltage of 29 V, concentration of acetic acid decreased and the current increased during the experiments.

b. Temperature affected the electrolysis process. As temperature increased (from 10 to 30°C), conversion of acetic acid increased as well.

c. Electrolysis of acetic acid resulted in formation of ethane, methane, hydrogen and carbon dioxide.

d. The maximum conversion achieved at 29 V was 11.9 % at 30ºC temperature over 8 hours of electrolysis.

e. Cost of treating 1wt% acetic acid aqueous solution with feed of 100 m^3/h with the conversion of 98.0% of acetic acid at 25ºC temperature over 8 hours was \$13.780/m^3. In the total cost, the operating cost was much higher than capital cost because of the cost of power.

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Chapter 6: Catalytic Decomposition

1. Introduction

The synthesis of ketones from carboxylic acids by ketonization has been known for long. In recent years, ketonization has received renewed attention for its potential application in the production and upgrading of renewable fuels and chemicals from conversion of cellulosic biomass [1]. The usefulness of this method of synthesis depends upon two factors: (1) the introduction of a carboxyl group at a desired site in the molecule by oxidation, and (2) the possibility of the removal of a carboxyl group under favorable circumstances [2]. A great improvement in ketone synthesis was the direct ketonization of carboxylic acids in the gas phase over solid catalysts under flowing conditions. Symmetrical, non-symmetrical and aralkyl ketones were obtained using this method. It is generally accepted that reducible amphoteric metal oxides, such as TiO_2, CeO_2, ZrO_2, and MnO_2, are the most effective catalysts for this reaction [3]. Oxides supported on inorganic carriers pumice, alumina, silica and titania or active carbon have been used [4]. General equation for the process of ketonization is as:

$$2RCOOH \rightarrow R - CO - R + H_2O + CO_2 \qquad \ldots 6.1$$

An analysis built upon a Langmuir–Hinshelwood (LH) model and transition state theory (TST) shows that the reaction follows a second-order expression with respect to the surface coverage of carboxylic acids [3].

The challenges associated with the treatment of Fischer-Tropsch acid water have been outlined before [5]. A different approach to the methods that were discussed in Chapters 3 to 5 is to prevent the formation of acid water. It stands to reason that if the carboxylic acids are converted into ketones as per equation 1.1 the wastewater after primary separation will be acid free. In this chapter it was investigated whether a ketonization process could be used as an alternative technique that is preventative instead of treating acid water after is has been produced.

Based on literature reports of the performance of different catalysts for ketonization [4], it was decided to perform a kinetic study of the ketonization of an aqueous solution of 1 wt% acetic acid using a 20wt% CeO_2/SiO_2 catalyst. In the presence of the CeO_2/SiO_2 catalyst, reactions were carried out at different temperatures to see the effect on concentration of acetic acid in water. The change in concentration of acetic acid in the solution was used to calculate rate of reaction. Although this study does not accurately mimic a Fischer-Tropsch reaction product, it approximates the main elements (water and carboxylic acids) that would be involved in competitive adsorption on the catalyst surface.

Based on the results a conceptual design was developed for cost evaluation of this technique. The design was developed using the same base case as for the other treatment methods, which were based on 100 m^3/h of 1wt% acid in aqueous solution. It is pointed out that although the implementation of this method is aimed at conversion of the vapor phase product directly after Fischer-Tropsch synthesis, the conceptual process was developed as an acid water treatment unit, to keep the comparison of methods on equal basis.

2. Experimental

2.1. Materials

Acetic acid ($C_2H_4O_2$, ≥99.7%), Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3.6H_20$, ≥99%) , Tetraethyl orthosilicate ($C_8H_{20}O_4Si$, ≥99%) and ethanol (C_2H_6O, ≥99.8%) were purchased from Sigma Aldrich. For titration standard solution of 1M sodium hydroxide supplied by Sigma Aldrich was used. Solutions were prepared in distilled water (conductivity around 3 µS/cm at 25°C) obtained from Milli-Q (serial no. F1PA 38231B) water purification system purchased from Millipore. Nitrogen (99.999 %) from Praxair was employed for pressurizing the reactor and providing an inert atmosphere.

2.2.Preparation of catalyst

Metal oxide CeO_2 over support SiO_2 was selected as catalyst for the process because it gave higher conversion of acetic acid [5]. Dry incipient technique was used to prepare the catalyst. An amount of 25.23 g of cerium (III) nitrate hexahydrate ($Ce(NO_3)_3.H_20$) was dissolved in ethanol to form a solution. 138.70 g of tetraethyl orthosilicate (TEOS, $C_8H_{20}O_4Si$) was then added to cerium (III) nitrate hexahydrate and ethanol solution drop wise under continuous stirring on a stirrer, producing a transparent gel. The produced gel was dried naturally overnight and then in an oven at 110°C till completely dry. The solution after drying formed light brown course granules. These granules were calcined in air at 700°C for 3 hours, giving 20wt% CeO_2 over SiO_2 catalyst.

2.3.Equipment and procedure

A 1wt% acetic acid solution was prepared by adding 1 g acetic acid to 99 g of distilled water. A solution of around 3000 g was prepared for each run of experiments. Weighing of solutions was done using Mettler Toledo MT ML3002E (0.01-3200g range, 0.01g readability) balance.

A fixed bed reactor system was designed, constructed and commissioned to perform experiments, shown in Figure 1. This was part of the scope of work reported in this chapter (see Section 2.4).

A general operation is as follows: The reactor was loaded with 50 g of 20wt% CeO_2 over SiO_2 catalyst. The reactor system was then pressurized to 3 MPa and leak tested. This was done by injecting nitrogen gas at 3 MPa from a nitrogen cylinder into the system. To maintain the whole system at this pressure, the pressure was controlled using a back pressure regulator. The feed (1wt% acetic acid aqueous solution) was weighed using weighing balance and was fed continuously at the rate of 2 ml/min to the system by using a pump. The liquid flow rate was verified by measuring the loss of weight of the feed tank per unit time. Once the feed to system was started, nitrogen flow for pressurization to system was turned off. A preheater (heating tape) was used to raise the temperature of the solution before it entered reactor. The temperature before and after preheater was checked continuously to monitor working of preheater. Heated feed then entered the reactor. The temperature of acetic acid aqueous solution in reactor was further increased by using furnace around the reactor. Temperature of the furnace was varied and maintained with the help of furnace controller. After reaction, which took place over the catalyst bed in the reactor, the high temperature product was cooled by passing reactor outlet through a chiller. Products were collected in a product tank. Liquid samples were taken after 2 hours gap of an 8 hour long experiment and analyzed. Gaseous product from the product tank was continuously analyzed online by passing it through CO_2 analyzer to determine the presence of CO_2. Temperature at different points of the setup was measured.

Experiments were performed to determine the effect of temperature on concentration change in 1wt% acetic acid aqueous solution. Material balance closure was generally within 97 to 103wt%. Four runs of experiments were carried out for four different reactor temperatures. For a reactor temperature, experiment was performed for eight hours. For each reactor temperature, results were reported as average.

2.4. Design of fixed bed reactor system

A fixed bed reactor system was designed and constructed to perform experiments in lab. It was designed for a constant weight of catalyst. The catalyst used was CeO_2/SiO_2 assuming bulk density of 0.8 g/ml, which is the same as the bulk density of SiO_2. Weight of catalyst taken was 50 g and all the calculations were done on this basis, presented in Table 6.1.

Table 6.1. Design calculation for fixed bed reactor system based on constant weight of CeO_2/SiO_2 catalyst of bulk density 0.8 g/ml. Weight hour space velocity (WHSV) used 2.4 g/g cat.h.

Weight of catalyst (g)	Vol. of catalyst (ml)	Vol. of catalyst (in^3)	Diameter of reactor (in)	Height of catalyst in reactor (in)	WHSV (g/g.h)	Flow rate (ml/h)	Flow rate (ml/min)
50.00	62.5	3.81	1.00	4.85	2.40	120	2.00

Figure 6.1 shows a simplified flow sheet of the fixed bed reactor system, which was designed to withstand pressures as high as 10.0 MPa. Equipment and instruments used to build reactor system are presented in Table 6.2.

Table 6.2. List of equipment and instruments used in constructing fixed bed reactor system, which was designed for a maximum pressure of 10 MPa.

Equipment/Instrument	Manufacturer	Model	Range
Pump	Scientific Systems Company	HPLC pump, Series I, 110SFN01	45W, 0-10 ml/min
Reactor	Swagelok	1 in. tubing	-
Furnace	Lindberg/Blue M	HTF55122A	120V, 11 A, 1.3kW
Chiller	Julabo	FP 50	-50 to 200°C
Pressure gauge	Swagelok	-	0-3000 Psi
Pressure relief valve	Swagelok	-	2250-3000 Psi
Back pressure regulator	TESCOM	26-1765-24-410	Upto 1500 Psi
Check valve	Swagelok	-	25 Psi cracking pressure
Product tank	Swagelok	304L-HDF8-2250	2250 cm^3
Weighing balance	Mettler Toledo	ML3002E	0.01-3200 g
Preheater	Omega	FGS series	Upto 482°C
Thermocouple	Omega	KMQXL-062U-12	Upto 1335°C
Weighing balance	Mettler Toledo	MT ML3002E	0.01-3200 g
CO_2 analyzer	Alpha Omega Instruments	Series 9600	0-5000 ppm CO_2

The reactor system was designed with future experimentation in mind. Although the current investigation entailed a vapor phase conversion, which is blind to the flow direction (top down, or bottom up), the flow direction matters for liquid phase reactions.

For this design flow direction in the reactor that was selected was up flow. Up flow was selected, because up flow reactors are often used in laboratory-scale studies, since complete catalyst wetting is ensured and better heat transfer (due to a continuous liquid phase) and higher overall liquid-solid mass-transfer coefficients can be achieved. Liquid-limited conditions result in better up flow performance over down flow [6]. It has been reported in the literature that small bench scale plants operating in the down flow mode can have a poor conversion compared to the commercial units. A poor contact between the liquid and the catalyst was reported to be at the origin of this phenomenon [7].

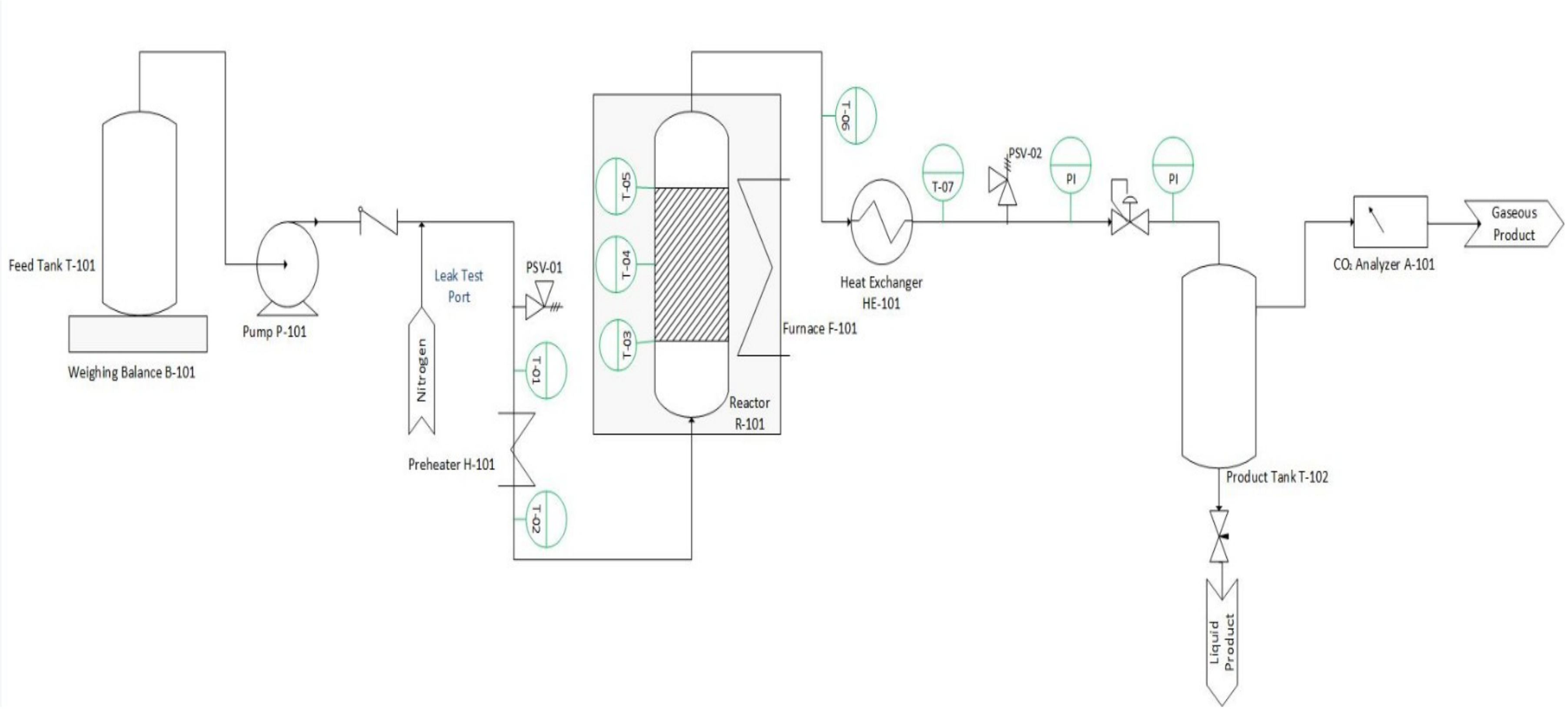

Figure 6.1. Process schematic diagram of pilot plant for fixed bed reactor system.

2.5.Analysis

Product liquid samples were analyzed for the concentration of acetic acid in water by titrating it against 1 M standard sodium hydroxide with phenolphthalein as indicator. Glass Burette (2 ml burette, 1/100 ml) from Fischer Scientific was employed for performing titration.

A Mettler Toledo (MT ML3002E, 0.01-3200 g, 0.01 g readability) weighing balance was used to weigh samples.

Liquid samples were checked for the presence of acetone using a Fourier Transform Infrared Spectroscopy (FTIR) from ABB MB3000 (Class 3B laser, 760 nm, 2mW). The FTIR was equipped with a Pike Miracle attenuated total reflectance (ATR) accessory.

Gaseous product was passed continuously through an on-line CO_2 analyzer (Alpha Omega Instruments, Series 9600, 0-5000 ppm CO_2) to detect presence of CO_2 in the product.

2.6.Conceptual design methodology

Heat requirements for the process design was calculated by modelling the system using the process simulation software Aspen plus. Thermodynamic model used was NRTL.

The reactor design was based on the experimental data obtained from the fixed bed reactor system. The experimental data was employed to develop a kinetic description of the reaction, which could then be used for reactor sizing by using the design equation for a plug flow reactor.

3. Results and Discussion

3.1.Rate of reaction

Reactions were carried out at different temperatures starting from 233 to 296°C internal reactor temperature. The reactor temperature was changed by varying temperature of the furnace. Concentration of acetic acid in product was determined at each temperature, presented in Table 6.3.

Table 6.3. Experimentally determined concentration of acetic acid in product from ketonization reaction at different reaction temperatures with initial concentration of 1wt% acetic acid over CeO_2/SiO_2 catalyst at 3MPa pressure and WHSV of 2.4 g/g cat.h.

Temp (°C)	Initial conct (wt%)	Final conct (wt%)	Avg Final conct (wt%)	Std Dev	Final conct (wt%)
233	1.000	0.9908	0.9908	0	0.9908
		0.9908			
		0.9908			
		0.9908			
243	1.000	0.975	0.975	0	0.975
		0.975			
		0.975			
		0.975			
258	1.000	0.9608	0.964	0.0071	0.964±0.0071
		0.975			
		0.9608			
		0.9608			
296	1.000	0.975	0.956	0.0144	0.956±0.0144
		0.945			
		0.9608			
		0.945			

As temperature in the reactor was increased, concentration of acetic acid in the product decreased showing that at higher temperatures more acetic acid in the feed is converted into product. From the change in concentration of acetic acid in water with temperature, reaction rate constant was calculated. Equation for plug flow reactor was used to calculate the rate of reaction and thus rate constant. Based on literature [3] the data was fit assuming a second order rate equation (Equation 6.2).

$$\tau = \frac{V}{V_o} = C_{AO} \int_0^{X_A} \frac{1}{-r_A} dX_A = C_{AO} \int_0^{X_A} \frac{1}{kC_A^2} dX_A \qquad \ldots 6.2$$

Where,

V, V_O = Active volume (L) and volumetric flow rate (L/s)
C_{AO} = Initial concentration (mol/L)
C_A = Final concentration (mol/L)
τ = Space time (s)
$-r_A$ = Rate of reaction (mol/L.s)
X_A = Conversion
k = Rate constant (L/mol.s)

The results from the calculations assuming a second order rate equation are presented in Table 6.4.

Table 6.4. Reaction rate constant calculated at different temperatures from experimentally determined conversion of acetic acid in 1wt% acetic acid aqueous solution feed assuming a second order reaction.

Temp (°C)	Final conct. (wt%)	C_A (mol/L)	Conversion, X_A	Space Time, τ (s)	k (L/s.mol)
233.6	0.991	0.165	0.009	1875	2.9×10^{-05}
243	0.975	0.162	0.025	1875	8.2×10^{-05}
258	0.964	0.161	0.036	1875	1.2×10^{-04}
296.7	0.956	0.159	0.044	1875	1.5×10^{-04}

It can be seen that at lower temperature conversion of acetic acid is less and as the temperature increases, conversion of acetic acid increases too. According to the Arrhenius equation (Eq. 6.2) with an increase in temperature of the reaction, the rate constant increases, resulting in increase in reaction rate, as shown in Figure 6.2.

Another reason can be found in the mechanism. Temperature programmed desorption studies of carboxylic acid decomposition on TiO_2 revealed that there are two adsorbed phases of carboxylic acid on TiO_2 at room temperature, which are the carboxylic acid (i.e. physisorbed) and carboxylate (i.e. chemisorbed) [8]. At temperatures lower than around 125°C, 40% of surface carboxylate recombined with surface hydroxyl group to form the parent carboxylic acid (Eq. 6.3), which could be desorbed as the acid. However, at higher temperatures, >250°C, the surface carboxylate formed the ketone by bimolecular ketonization (Eq. 6.4), e.g. acetone from acetic acid.

$$k \propto e^{-E/RT} \qquad \ldots 6.2$$

where,

k = Rate constant
E = Activation energy
R = Gas constant
T = Temperature

$$RCOO_{ad} + OH_{ad} \rightarrow RCOOH_g + O_l \qquad \ldots 6.3$$

$$2RCOO_{ad} \rightarrow RCOR_g + CO_{2\,ad} \qquad \ldots 6.4$$

Where g and ad denote gaseous phase and adsorbed phase and O_l denote lattice oxygen.

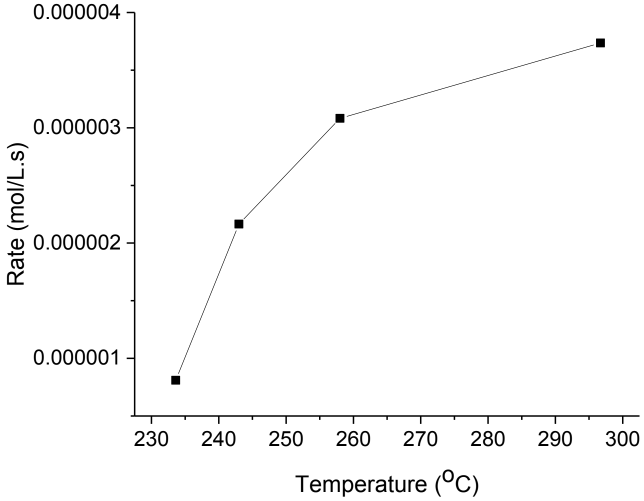

Figure 6.2. Influence of temperature on rate of ketonization of 1wt% acetic acid aqueous solution over CeO_2/SiO_2 catalyst at 3MPa pressure, WHSV = 2.4 g/g cat.h.

For a 20% CeO_2/SiO_2 catalyst it was reported that a conversion of around 31% could be obtained at 300°C, this is the lowest ketonization temperature reported in literature [5].

In our work that employed a 20% CeO_2/SiO_2 catalyst prepared as was outlined, the conversion was only 4.4% at 296.7°C.

The huge difference in conversion is likely due to mass transport limitations, although the low fluid velocities, fluid dynamics, and mass transfer phenomena may also have had an impact on the obtained conversions [10].

According to the Arrhenius law, a plot of inverse temperature (1/T) against rate constant (k) should be a straight line with negative slope (Eq. 6.2). However, in our work the slope was not straight, as shown in Figure 6.3. This could be because of mass transfer limitations. The concentration gradient at the catalyst can affect the kinetics of the reaction. The concentration gradient could be at three domains: a) Intraparticle within catalyst particles; b) Interphase between the external surface of the particles and fluid adjacent to them; and c) Interparticle between the fluid regions or catalyst particles. Resistance to transport of reactant to catalyst in any domain can affect the experimental results.

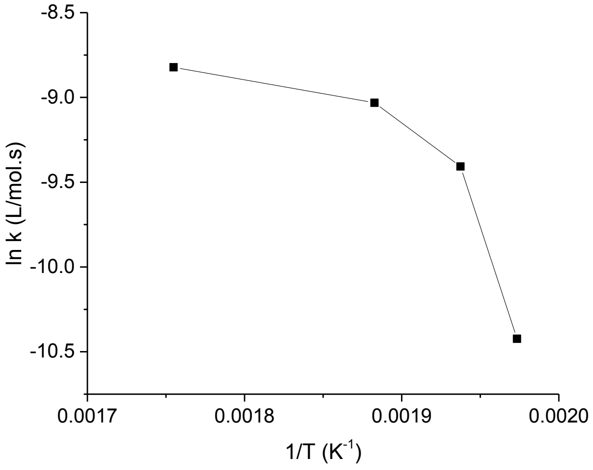

Figure 6.3. Temperature inverse plotted against reaction rate constant for ketonization reaction of 1wt% acetic acid aqueous solution over CeO_2/SiO_2 catalyst at 3MPa pressure, WHSV = 2.4 g/g cat.h.

3.2. Confirmation of products

As per Eq. 6.1, the products from ketonization of acetic acid should be acetone, CO_2 and H_2O. The presence of CO_2 in product gaseous stream was detected by using CO_2 analyzer. Results of CO_2 analyzer showed an increase in the CO_2 concentration (around 535 to 954 ppm) as compared to atmospheric CO_2 (around 300 ppm).

For determining presence of acetone in liquid product, FTIR was used. From FTIR results it could not be confirmed that there was acetone present in the liquid product. It is likely that the acetone was stripped out of the liquid, or present in too low concentration to be detected.

3.3. Conceptual design

A conceptual design was developed for cost evaluation. System was designed for a maximum pressure of 3 MPa. Figure 6.5 shows the conceptual design. A pump P-101 was used to pump the feed into the pressurized system. In the design, feed enters system through heat exchanger HE-101, where feed is heated by heat transfer with reactor outlet. After the heat exchanger, the heated feed enters furnace F-101, where temperature of feed is further increased to reaction temperature. Reactor R-101 is loaded with 20wt% CeO_2/SiO_2 catalyst. Around 10% volume of reactor was assumed is for reactor internals. After the reaction in reactor, the product was passed through heat exchanger HE-101 to heat feed. Another heat exchanger HE-102 is used after HE-101. In HE-102, water is converted into steam by using heat from the HE-101 hot outlet stream as it is still at high temperature.

The setup was designed for 3 MPa therefore cost has been calculated for this pressure.

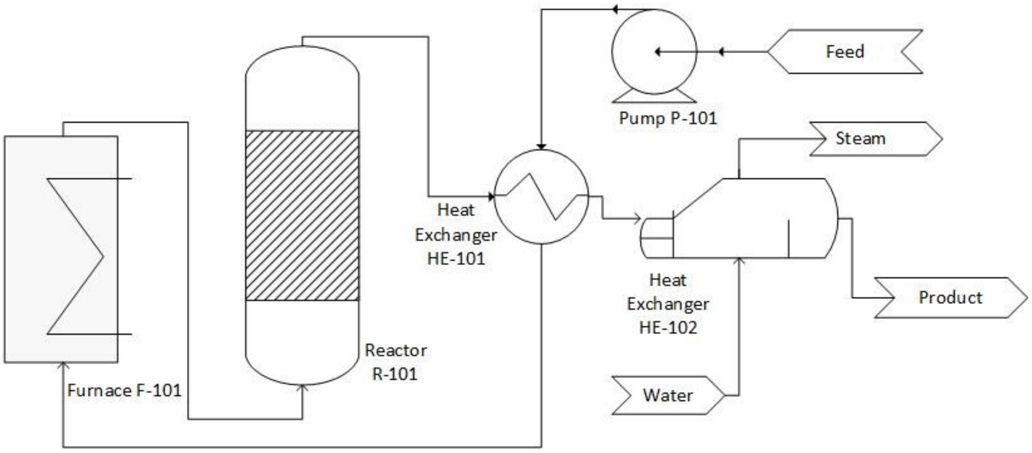

Figure 6.4. Conceptual design for ketonization reaction of 1wt% carboxylic acid aqueous solution over CeO_2/SiO_2 catalyst.

3.4.Cost evaluation

Assumptions made for calculating cost have been outlined in Chapter 3 section 3.1. Cost evaluation for treating 100 m^3/h of 1wt% acetic acid aqueous solution by ketonization was done on the basis of kinetics from literature [3].

3.4.1.Capital cost

Total capital cost was calculated by determining capital cost of each equipment.

a. Reactor

Capital cost of reactor was determined on the basis of its dimensions. Reactor was assumed to be working at 3 MPa maximum pressure. The results achieved from experiments were only upto 296°C and there was mass transport limitations due to which the Arrhenius plot was not a straight line. Therefore, the kinetics from literature was used for conceptual design. The dimensions of the reactor were calculated from reaction kinetics determined from literature, as shown in Eq. 6.5 [3].

$$rate = k\frac{(K_{RCOOH}P_{RCOOH})^2}{(1+K_{RCOOH}P_{RCOOH}+K_{RCOR}P_{RCOR}+K_{CO_2}P_{CO_2}+K_{H_2O}P_{H_2O})^2} \qquad \ldots 6.5$$

Where,

k = Rate constant (mol/g cat.h)

$K_{RCOOH}, K_{RCOR}, K_{CO_2}, K_{H_2O}$ = Adsorption constants for acetic acid, acetone, carbon dioxide and water, respectively (Torr^{-1})

$P_{RCOOH}, P_{RCOR}, P_{CO_2}, P_{H_2O}$ = Partial pressure of acetic acid, acetone, carbon dioxide and water, respectively (Torr^{1})

The rate expression was determined at 3MPa using Eq. 6.5. Adsorption constants were used form the literature and partial pressure of components were calculated and Eq. 6.5 became as follows with units of mol/g cat.h:

$$r = 7.8 \times 10^{-5}(1-X)^2 \qquad \ldots 6.6$$

In the literature, experiments were performed for temperature upto 285°C [3]. Using the activation energy (E_a = 156 kJ/mol) at this temperature from the literature resulted in small rate constant which in turn lead to huge active volume. Therefore, activity of the catalyst needed to be increased so as to get a more realistic active volume. A temperature was selected that increased the rate constant as per Arrhenius equation (Eq. 6.2). At 350°C, the value of rate constant calculated was $2.6\text{x}10^{-2}$ mol/g cat.h. resulting in a more realistic active volume. The active volume was calculated using plug flow reactor design equation (Eq. 6.7) for the conversion of 98%.

$$\int_0^V dV = \frac{F_{in}}{k}\int_0^{0.98} \frac{1}{(1-X_A)^2} dX_A \qquad \ldots 6.7$$

Where,

F_{in} = Molar flow rate (mol/h)

X_A = Conversion

V = Active volume (g cat)

Dimensions of reactor were calculated from active volume. Height to diameter ration of reactor was kept >4 [10]. It was assumed that 10% of reactor was for reactor internals. Results are presented in Table 6.5.

Table. 6.5. Dimensions of catalytic bed reactor calculated on basis of kinetics from experiments for plug flow reactor.

C_{AO} (mol/L)	X_A	Vol (m^3)	Vol of reactor (m^3)	Diameter (m)	Height (m)
0.167	0.98	312	429	4	34.2

WHSV was then calculated from the active volume of reactor taking bulk density of catalyst 0.8 g/ml and feed rate of 100 m^3/h as shown in Table 6.6.

Table 6.6. Calculated WHSV for feed rate of 100 m^3/hr and catalyst density 0.8 g/ml.

V (m^3)	Mass of Cat (Ton)	WHSV (g/g cat.h)
390	312	0.320

b. Heat exchanger

Using process simulation software Aspen plus, area of heat exchanger HE-101 was determined. Thermodynamic model NRTL was employed and all the streams of heat exchanger were at 3 MPa pressure. For simulation, with cold stream inlet (feed) at 25°C, temperature, cold stream outlet temperature was fixed and area required for heat exchange was determined. This way it was determined to what maximum temperature cold stream outlet temperature could reach so that area of heat exchanger is economical.

The feed, when it enters the heat exchanger, is at 25°C, 3MPa and in liquid phase. At 3MPa, bubble point of 1wt% acetic acid in water solution is around 234.2°C, as determined from Aspen plus simulation software using NRTL thermodynamic model. Keeping pressure same as 3 MPa, when feed is heated in heat exchanger to 234°C, it is still in liquid phase. On the other hand, hot inlet of heat exchanger is at 350°C and therefore in vapor phase. During heat transfer, amount of heat released during condensation of hot stream is used to heat the cold stream. Because of this restriction of bubble point temperature of the feed, it could only be heated to 234°C with realistic heat exchanger area.

Table 6.7 present the results of simulation.

Table 6.7. Area of heat exchanger HE-101 determined using Aspen plus employing NRTL thermodynamic model at 3 MPa pressure with feed (cold inlet) at temperature of 25°C.

$T_{hot,in}$ (°C)	$T_{hot,out}$ (°C)	$T_{cold,in}$ (°C)	$T_{cold,out}$ (°C)	Heat exchange area (m^2)	Bubble point (1wt% acetic acid in water), (°C)
350	234.1	25	234	373	234.2

Since HE-101 hot stream temperature outlet was still around 234°C, it was used to generate steam with the help of another heat exchanger (kettle reboiler), HE-102. Aspen plus simulation software with thermodynamic model NRTL was employed to calculate the area required for heat exchange. Boiling temperature of water at 2 MPa is around 212°C [11]. Steam, at 2MPa pressure, of around $3x10^3$ kg/h was generated.

Since there is not much heat transfer in the HE-101 due to the bubble point of 1wt% acetic acid in water, more heat can be recovered in the form of low pressure steam by having low temperature HE-101.This is not included in the conceptual design.

c. Total capital cost

The total capital cost of treating 1wt% acetic acid aqueous solution was done by summing up capital cost of each equipment. Table 6.8 shows the total capital cost of treatment per m^3 of feed.

From Table 6.8, total capital cost over 20 years plant life with stream factor of 95% = $1.42/$m^3$.

Table 6.8. Capital cost summary of conceptual design for ketonization of 1wt% acetic acid aqueous solution operating at 10 MPa maximum pressure. Lang factor 3 and cost index for year 2004 and 2013 used 400 and 480, respectively. Plant location Canada, currency in US dollars for the year 2013.

Eqiupment Identification	**Number**	**Capacity or size specifications**	**Purchased equipment cost (base material)**		**Actual bare module factor, F^a_{BM}**	**Actual bare module cost, C^a_{BM}**	**Total (million $)**
			Year 2004	Target year			
Feed Pump	P-101	Centrifugal, Stainless steel, 11.68 kW shaft power	9.0x10^3	10800	8	8.64x10^4	0.259
Furnace	F-101	4.1 m ID x 38 m vertical	1x10^5	120000	1.5	1.8x10^5	0.540
Catalyst			1.4x10^6	1680000	-	1.68x10^6	1.680
Reactor	R-101	4 m ID x 34.2 m vertical, Stainless steel, 3 Mpa	2x10^5	240000	12	2.88x10^6	8.640
Heat exchanger	HE-101	358 m^2, Shell and tube, Stainless steel, 3 MPa	1.5x10^5	180000	6	1.08x10^6	3.240
Heat exchanger	HE-102	98 m2, Kettle reboiler, Stainless steel, 2MPa	3.5x10^4	78000	4.5	3.51x10^5	1.053
Total bare module cost (million $)						C_{TBM}	15.412
Total module cost (million $)						$C_{TM} = C_{TBM}$x1.18	18.186
Auxiliary cost (million $)						$C_A=C_{TM}$x0.30	5.456
Total capital cost (million $)						$C_T = C_{TM}+ C_A$	23.642
Total capital cost over 20 years plant life with stream factor of 95% ($/$m^3$)[a]						C_T	**1.420**

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[a] The capital cost was converted to an operating cost per m^3 feed processed, assuming a discount rate of 0%.

3.4.2.Operating cost

a. Pump

From calculated shaft power of 11.68 kW, operating cost of pump calculated using natural gas price of US$5/GJ for generating electricity with efficiency of 0.4. Calculated operating cost for pump was $0.005/m^3.

b. Furnace

Operating cost for furnace was calculated from the amount of energy required to raise the temperature of feed to reaction temperature. Amount of energy required to heat the feed from heat exchanger temperature outlet (234°C) to reaction temperature (350°C) was 13.6 MW. Heating was done using natural gas. Therefore, cost of treating per m^3 of feed was $2.436.

c. Steam generated

Employing HE-102, steam was generated by using heat from HE-101 hot stream outlet which was at 234°C. Steam of around 3×10^3 kg/h at 2MPa was generated. This steam can be used in the process plant for heating, etc. Cost of this generated steam was calculated [10]. Steam worth of $0.276/m^3 was generated for treating feed of 100 m^3/h of 1wt% acetic acid aqueous solution.

3.4.3.Total treatment cost

Total cost of treating 1m^3 of 1wt% acetic acid in water to the final concentration of acetic acid (200mg/L) in product aqueous solution at 350°C with WHSV = 0.320 g/g cat.h is $3.585/m^3.

4. Conclusion

Ketonization reaction was studied for treatment of Fischer Tropsch aqueous product effluent, also called acid water. Ketonization of acetic acid was carried out, using a feed containing 1wt% acetic acid aqueous solution, over 20wt% CeO_2/SiO_2 catalyst to reduce the concentration of acetic acid in the product. The maximum temperature to which experiments were performed was 296°C. From this work, it can be concluded:

a. Decrease in concentration of acetic acid in 1wt% acetic acid aqueous solution occurred over 20wt% CeO_2/SiO_2 catalyst.
b. At different temperatures, decrease in concentration of acetic acid was different. Conversion of acetic acid was higher at high temperature as compared to low temperatures. Therefore, rate of ketonization reaction increased with increase in temperature.
c. There was presence of CO_2 in the gaseous product but acetone was not detected in the liquid product. It may be because acetone is in low concentration or is stripped off.
d. The experimental results didn't follow the Arrhenius equation. This could be because of the mass transport resistance to reactants from bulk fluid to catalyst.
e. The maximum conversion of 4.4% of acetic acid achieved was at temperature of 296°C.
f. To have a more realistic design, temperature of the operation had to be higher than that used for experiments. Using reaction kinetics form literature, the temperature selected for the design was 350°C, as at this temperature activity of catalyst was increased and thus active volume was realistic too.
g. Total treatment cost per m^3 of 1wt% acetic acid aqueous solution for 98.9% conversion of acetic acid was around US$3.585. During the ketonization by using conceptual design, steam at low pressure (2 MPa) was generated which is an operating expenditure income.

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Chapter 7: Comparative Evaluation and Conclusion

1. Introduction

The overall objective of the two year research was to find an alternative technique for treating Fischer-Tropsch acid water that is suitable for application in Canada. The technique had to be technically and economically viable. The current industrially applied methods of treating Fischer-Tropsch acid water by conventional biological treatment (aerobic and anaerobic) was studied as base case and cost estimation was done (Chapter 3). The three main techniques that were identified as potential alternatives were Fractional freezing, Electrolysis and Catalytic decomposition. These processes were investigated as alternative techniques for treating Fischer-Tropsch acid water (Chapters 4, 5, and 6). Each was evaluated experimentally and for each a conceptual design and cost estimation was prepared on the same basis as for biological treatment. The comparison of the fractional freezing, electrolysis and catalytic decomposition to the base case biological method is done in this chapter. The main points from their comparison and conclusion are summarized below.

2. Comparison to base case

The comparison of the techniques used to treat Fischer-Tropsch acid water was done on the basis of economics. Table 7.1 shows the comparison.

Table 7.1. Comparison of Biological, Fractional freezing, Electrolysis and Catalytic decomposition methods of treating 100 m^3/h of Fischer-Tropsch acid water containing 1 wt% carboxylic acids at 25°C and near atmospherics pressure at a Fort McMurray Canada location with a 2013 cost basis in US dollars.

Method of treatment		**Capital cost ($/$m^3$)**	**Operating cost ($/$m^3$)**	**Total cost of treatment ($/$m^3$)**	**Operating income ($/$m^3$)**	**Net cost ($/$m^3$) [a]**
Biological	Aerobic	1.259	0.43 - 0.45	1.689 - 1.709	0	1.689 - 1.709
	Mesophilic	1.694	0.528 - 0.537	2.222 - 2.231	1.025	1.197 - 1.206
	Thermophilic	1.528	0.605 - 0.613	2.133 - 2.141	1.025	1.108 - 1.116
Fractional Freezing		0.309	6.513	6.822	3.46 - 10.79	3.362-(-3.968)
Electrolysis		2.176	11.604	13.78	0	13.78
Catalytic decomposition		1.420	2.441	3.861	0.276	3.585

[a] Negative values imply a net income, positive values a net cost.

From the Table 7.1, it can be concluded that conventional techniques, biological methods, treats the acid water at the lowest treatment cost. Although, anaerobic processes (mesophilic and thermophilic) are more expensive than aerobic treatment, the anaerobic methods generate methane during the treatment, which has energy value. Income from methane can reduce the net treatment cost.

Fractional freezing has the potential to be used as an alternative technique to treat Fischer-Tropsch acid water. Carboxylic acids (acetic acid, propionic acid and butyric acid) recovered during the treatment. Since these acids have market value, an sales income of around 3.46 to 10.79 was generated, depending on the type of acid (around acetic acid = \$8, propionic acid = \$10.7, butyric acid = \$3.4). The concentration of butyric acid in Fischer-Tropsch acid water is small as compared to propionic acid and acetic acid, as outlined in Chapter 3. Overall this process can be profitable depending on the acid composition.

Electrolysis was the most expensive technique to treat Fischer-Tropsch acid water. The process treated the acid water but had no product income to balance the treatment cost. Its operating cost was quite high. This was due to electric power provided to the system for electrolysis. Therefore, the possibility of using this technique for treating Fischer-Tropsch acid water is quite low.

Catalytic decomposition of treatment was expensive compared to the biological method. Operating cost of the processes was high as compared to capital cost because of the need to heat the feed with furnace. However, product income was generated by producing low pressure steam during the process. Increased product income can be generated by more exhaustive heat recovery by using additional heat exchangers for generating more steam, which can reduce total operating cost at some incremental capital cost. This process can also be integrated directly downstream from Fischer-Tropsch synthesis, which might reduce the heating cost.

3. Major conclusions

The major conclusions from this work are as follows:

a. Biological method of treating Fischer-Tropsch acid water is current industrial practice. The main challenge with this technique for application in Canada is the temperature at which microorganisms grow. For cold temperature regions, feed needs to be heated for the process to be effective, this in turn increases its operating cost.
b. Three alternative processes for treating acid water could be proposed: fractional freezing, electrolysis and catalytic decomposition.
c. Fractional freezing is a technique that is suited for colder regions, like Northern Canada. As this technique utilizes freezing, low ambient temperatures is helpful. However, during summers, when ambient temperature is on the positive side of temperature scale (^{o}C), heat needs to be removed from the feed, which increases the operating cost.
d. An experimental evaluation of the solid-liquid equilibria of 1 wt% acetic, propionic and butyric acids in water was conducted. The values were close to data previously reported in literature. As freezing was continued to the eutectic point of carboxylic acids, an increasing percentage of solids (ice crystals) were formed which is pure water and met the criteria for environmental discharge.
e. From the conceptual design study it was determined that the optimum temperature at which fractional freezing should be performed is -5^{o}C. At this temperature, the total amount of energy required for the process is at its lowest.

f. During fractional freezing, rather consuming/destroying carboxylic acids, they are recovered. Since the acids have market value, selling them could not only cover the total cost of treatment, but it can be profitable as well.

g. Electrolysis of 1 wt% acetic acid in water resulted in a decrease in acetic acid concentration in product. During the experimental study the maximum conversion of acetic achieved was 11.9% at 30°C over an 8 hours with constant voltage of 29 V and electrode area of 3.3×10^{-3} m^2. The operating temperature range investigated was 10 to 30°C.

h. The product formed by electrolysis of 1wt% acetic acid in water were methane (CH_4), ethane (C_2H_6), carbon dioxide (CO_2) and hydrogen (H_2). There was an increase in concentration of CO_2 with time and with increase in CO_2, H_2 increased as well.

i. A laboratory flow reactor system was designed, constructed and used to evaluate a self-prepared ceria/silica catalyst for catalytic decomposition. A maximum conversion of 4.4% of acetic acid was achieved during the experimental catalytic decomposition study, which was conducted over the temperature range 233 to 296°C, 3 MPa and weight hourly space velocity of 2.4 g $(g_{cat})^{-1}h^{-1}$. These results were below the values reported in literature and the literature data was employed for the conceptual design.

j. For the conceptual design a temperature of 350°C was selected (using kinetics from literature). At these conditions the value of rate constant was 2.6×10^{-2} mol/(g cat).h. Steam can be generated during the process, which is a product income, but not sufficient to cover the high operating cost.

k. Of the three alternative methods for dealing with Fisher-Tropsch acid water, the process that is the most competitive with biological treatment, is fractional freezing.

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