Full Length Article

Fischer–Tropsch acid water processing by Kolbe electrolysis

Nuvaid Ahad, Arno de Klerk*

Department of Chemical and Materials Engineering, University of Alberta, 9211–116th Street, Edmonton, Alberta T6G 1H9, Canada

ABSTRACT

Fischer–Tropsch synthesis produces roughly equal amounts of water and oil as products. The water product is acidic due to dissolved carboxylic acids. Treating this acid water in small-scale facilities designed for remote locations is a challenge, because conventional biological treatment might be impractical. Kolbe electrolysis was investigated as potential process for acid water treatment in such small-scale facilities. The Kolbe electrolysis of acetic acid in dilute aqueous solution produced methane, ethane and CO_2 as expected. However, current efficiencies in the operating range 10–30 °C were less than 3% and the energy required for acetic acid conversion was > 2 GJ/kg acid. Hydrogen was co-produced by water electrolysis and the overall current efficiency of acetic acid and water electrolysis was of the order 20%. Despite being technically viable, it appeared unpromising compared to alternative electrolysis processes for use in small-scale remote Fischer–Tropsch facilities.

1. Introduction

Fischer–Tropsch (FT) synthesis is a technology that is employed for the conversion of synthesis gas into hydrocarbons and oxygenates [1]. Industrial facilities using this technology make use of either coal, or natural gas as raw materials to produce the synthesis gas, but synthesis gas can in principle be produced from other carbon-based feed materials too, such as biomass and organic waste. The main reaction that is taking place during FT synthesis is represented by Eq. (1).

$$CO + 2H_2 \rightarrow -(CH_2)- + H_2O \tag{1}$$

Although Eq. (1) does not capture the complexity of FT synthesis, it shows that hydrocarbon chain growth takes place in parallel with the formation of water. Water produced during FT synthesis is condensed and phase separated from the oil as part of product work-up after the reactor (Fig. 1). The composition of the aqueous product is governed by vapor–liquid–liquid equilibrium. The short carbon chain oxygenates that are produced during FT synthesis, are more polar in nature and preferentially dissolve in the aqueous phase. Compounds typically found in the FT aqueous product are C_1–C_5 alcohols, aldehydes, ketones, and carboxylic acids. The concentration and composition of oxygenates in the FT aqueous product is determined by the type of FT technology [1,2].

The light oxygenates with lower boiling points less than water, such as C_1–C_3 alcohols and carbonyl compounds can be recovered from the FT aqueous product by distillation. The bottom product from such distillation is water with < 2 wt% oxygenates [2,3]. The most abundant oxygenate class in this aqueous bottom product is carboxylic acids and this bottom product is appropriately called FT acid water. The FT acid water is a major product from FT synthesis and its flow rate is of the same order of magnitude as that of the oil product.

Industrial FT facilities treat the acid water as a wastewater and employ biological treatment in combination with other treatment steps to clean the water for reuse or discharge to the environment [1–5]. Suggestions to intensify such treatment by using biological treatment in combination with electrolysis have also been made [6,7]. Although biological treatment is an effective FT acid water treatment strategy for large-scale facilities, it might not be practical for small-scale FT facilities. The development of small-scale FT facilities have some unique challenges, which are associated with remoteness of location and accessibility [8], which could benefit from FT acid water treatment that do not rely on biological treatment. For such small-scale applications, electrochemical processes hold benefit, for example, electrodialytic recovery of carboxylic acids from acid water [9].

In this work the potential use of Kolbe electrolysis for the conversion of carboxylic acids in FT acid water was evaluated.

Kolbe electrolysis has found widespread application in organic synthesis [10–12]. The Kolbe electrolysis reaction is not an oxidation of the carboxylic acid itself, but rather of the carboxylate. The reaction proceeds stepwise [13], and can be written as (Eqs. (2) and (3)):

$$R-COO^- \rightarrow R-COO^{\cdot} + e^- \tag{2}$$

$$R-COO^{\cdot} \rightarrow R^{\cdot} + CO_2 \tag{3}$$

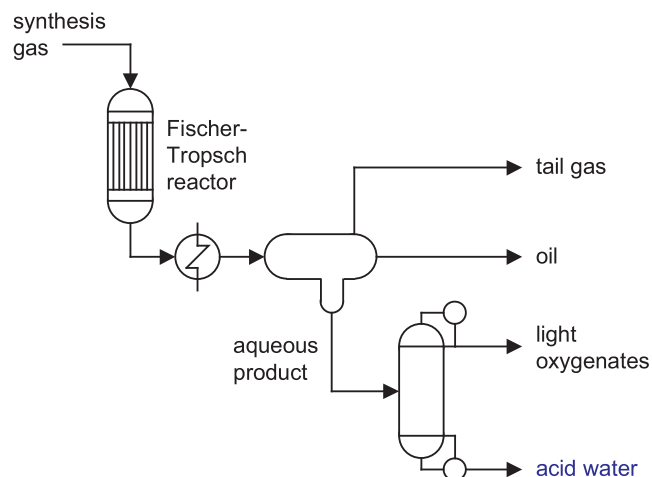Combination of the free radicals ($R^{\cdot}$) formed by electrolysis is the Kolbe pathway (Eq. (4)).

Fig. 1. Simplified flow diagram of a Fischer–Tropsch process to show the origin of Fischer–Tropsch acid water.

$$2 \, R^{\cdot} \rightarrow R\text{–}R \tag{4}$$

The free radical intermediates can also be oxidized to produce a carbocation (Eq. (5)) that leads to a different reaction pathway for product formation, which is referred to as the non-Kolbe pathway.

$$R^{\cdot} \rightarrow R^{+} + e^{-} \tag{5}$$

The selectivity to either the Kolbe pathway, or to the non-Kolbe pathway, can be manipulated through the current density, type of electrode employed and the solvent environment [14,15]. Of relevance to the present study is that the Kolbe pathway is favored by high current density.

Performing electrolysis of FT acid water can also lead to water electrolysis. It was reported that at high anode potential water electrolysis is suppressed and as Eberson [10] puts it: "This is probably the reason why the plug-into-the-wall variety of the Kolbe electrolysis is so successful." It was this type of high anode potential Kolbe electrolysis that was investigated for the treatment of FT acid water.

Since the aim was to evaluate Kolbe electrolysis for industrial application, some pragmatic decisions were taken with respect to the electrode materials based on cost. Although it is known that the Kolbe pathway is favored by a platinum anode [14], it was considered unlikely that a water treatment process employing platinum electrodes would be an economically viable proposition. Carbon was selected as anode material, even though a carbon anode would favor the non-Kolbe over the Kolbe pathway.

2. Material and methods

2.1. Materials

A 1 wt% acetic acid in water solution was employed to mimic high temperature Fischer–Tropsch acid water. This model solution disregarded heavier acids that would also be present [1,3], in order to simplify the reaction medium for study. The acetic acid (99.7%) was purchased from Sigma Aldrich. For titration 1 M standard solution of sodium hydroxide supplied by Sigma Aldrich was used. Solutions were prepared in purified water (conductivity ~3 µS/cm at 25 °C) from a Millipore Milli-Q purification system. Nitrogen (99.999%) was purchased from Praxair and it was employed to provide an inert atmosphere.

2.2. Methods

For each experiment 500 g of 1 wt% acetic acid in water solution

was prepared by adding 5.00 g of acetic acid in 495.00 g water. The solution was prepared by weight using Mettler Toledo ML3002E balance (0.01–3200 g range, 0.01 g readability).

A 500 ml glass round bottom flask with four arms (i.e. 5 connectors) was filled with the prepared solution of 1 wt% acetic acid. The anode was a carbon electrode (0.7 cm diameter, 7 cm submerged length), supplied by Fischer Scientific. The cathode was a 99.99% pure lead electrode (0.5 cm diameter, 8 cm submerged length), supplied by Alfa Aesar. A glass body calomel reference electrode from Fischer Scientific was used as reference electrode. A constant potential of 29 V with respect to the reference electrode was applied to the anode, which was the working electrode. The operating potential difference was based on reports in literature [10]. The potential difference was controlled using a direct current power supply from Keysight Technologies (U8032A, triple outlet, 60 V/3 A, with variability for constant voltage of ≤0.25% + 15 mV, and variability for constant current of ≤0.30% + 15 mA). The glass flask was placed in the fluid bath of a chiller, Julabo F25-ED chiller (temperature control to ± 0.03 °C). A constant temperature was maintained at either of 10, 20, 25, or 30 °C, which were the different temperatures investigated. These temperatures were selected in line with the intended application. Nitrogen flow was maintained using a variable area flowmeter at 17.5–20 mL/min and the gaseous product from the electrolysis was analyzed by a mass spectrometer (Extorr model PM Z01 300) connected to a T-junction in the off-gas line. The experimental setup is shown in Fig. 2.

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.

Safety note: It is important to maintain nitrogen flow during the experiment, due to the evolution of hydrogen and oxygen from water electrolysis, which is an inevitable side-reaction. The nitrogen flow rate should be sufficient to keep the product gases at low concentration so that the mixture is maintained below its lower explosive limit.

3. Results and discussion

3.1. Effect of temperature on conversion

The operating temperature at which electrolysis is conducted is important, because it affects the rate of carboxylic acid conversion. The water temperature also affects the operating cost when the water must be kept warm or heated up, as would be the case for water treatment in an arctic climate.

The first series of experiments to determine the effect of temperature on acetic acid conversion were performed in triplicate, so that the variability in the results for repeat experiments could be determined. The results of these experiments are presented in Table 1.

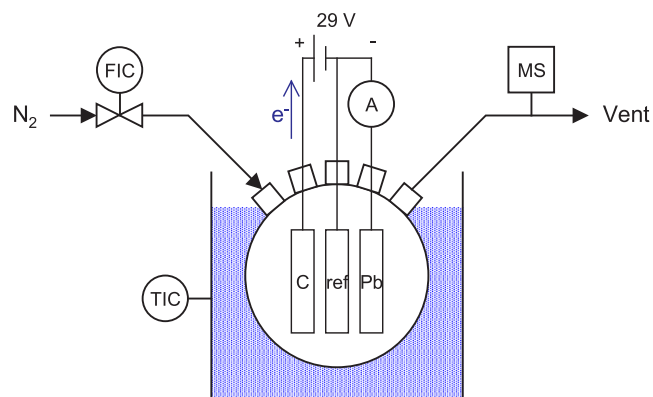Electrolysis at 10 °C resulted in no detectable conversion after 2 h.

Fig. 2. Experimental setup (TIC = Temperature indicating controller; FIC = Flow indicating controller; MS = Mass spectrometer; A = Current measurement).