

THE ACETIC ACID PRODUCTION BY MODELING OXIDATION OF ETHYLENE WITH ASPEN PLUS

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Abstract

This study investigates the design and optimization model of acetic acid production by oxidation of ethylene using Aspen Plus software. The input to simulation process is the vapor feed stream with CO₂, N₂ as bottom stream and H₂O as top input stream. The research aims to understand and study the production process of acetic acid and study the operational variables and their effects on the production. According to simulation model, the acetic acid has been produced as liquid in bottom stream after six stages inside absorber. Moreover, the flow rate, temperature and pressure have been controlled and analyzed as sensitivity parameters. The basic product is acetic acid produced with mole flow about 0.6 kmol/hr and the mole fraction about 0.004 at 30.3 °C temperature and 10 bar pressure.

Keywords: *Acetic acid, simulation, Aspen Plus, sensitivity analysis, modeling.*

Introduction

Acetic acid, is one of most important chemical compounds in our life, which is known by the special odor and sour taste. In fact, that sour taste comes from vinegar, which nearly from 4 to 8% are acetic acid. Before recorded history of humans, acetic acid has been producing and utilizing. As same as its taste, the name is coming from the Latin of vinegar, acetum as well. The acetic acid structure has been investigating, and controlled as chemical form (CH₃COOH) in the gas state by infrared spectroscopy and electron diffraction [1-3]. Generally, vinegar is created by dilute solutions of alcohol like wine, by the action of certain bacteria in the oxygen. To finish process bacteria, require oxygen while overall chemical change is the reaction of ethanol with oxygen to form acetic acid and water as showing in equation 1:



The acetic acid has several useful effects to human. Mineral deposits are left when the hard water evaporates. Then vinegar is used to remove the residue formed on plumbing fixtures and also that in tea kettles, dissolve in acids. In addition, vinegar is inhibiting the bacteria growth, so vinegar is utilized as a preservative in foods because it is acidic, like pickled vegetables, and as a mild disinfectant in cleaning. Although of their importance, the acetic acid (CH₃COOH) is known as one of simplest organic carboxylic acid. Acetic acid as colorless acid features by distinctive sour taste and pungent smell. In industry today, the acetic acid is considering as one of the industry keys for a lot of industries that contain chemical, detergent, wood and food industries as well. Utilizing petrochemical feedstock the acetic acid, chemically produced. Classic ways, by approach of fermentative alcohol conversion utilizing especial kind of acetic acid bacteria. In addition, methanol carboxylation is the most common production methods among several chemical techniques, which accounting about 65% of international

capacity [2]. Ethylene oxidation comes as second place, which is then followed by alkane oxidation processes. These days, acetic acid is one of the most an important component for the industrial production of various chemicals like cellulose acetate, vinyl acetate polymer, dimethyl terephthalate, acetic acid esters or acetic anhydride and calcium magnesium acetate [2].

In 1960 by BASF, it was the first commercial carbonylation process that includes conversion of methanol into acetic acid. The production of acetic acid in ca. with 90% selectivity, has been done utilizing iodide promoted cobalt catalyst with so high pressure (600 atm) and temperature (2300°C) [4]. The Cativa process, producing the acetic acid utilizing the iridium catalyst unit, which has been commercialized in 1996 by BP-Amoco [5]. By Wang et al., utilized catalysts to synthesis and production acetic acid by ethylene oxidation [4]. Nowadays, in industry, water and acetic acid separation process is one of the most important operations, as cellulose acetate production or in the terephthalic and isophthalic acids synthesis processes [6]. In addition, most of acetic acid production comes from distillation processes. In other words, it is the separation process that separates several components of a liquid solution, which depends on boiling points of the components. That process is done between liquid phase and vapor phase where all components are present in both phases. By boiling, the vapor phase is generated by liquid phase due to vaporization [7]. In chemical industries, acetic acid is important commodity, in fact per year nearly 9 million tons of world demands. In 1997, acetic acid has the demand about 5.4 million tons/year in the World [8]. Main utilize of acetic acid is manufacture of assorted acetate esters, organic compounds and solvents, fungicide as well as preparation of pharmaceuticals. In addition, acetic acid produces the cellulose acetate, which is significant in made film and plastic wares, synthetic fiber and perfumes. As corrosive organic, acetic acid (CH₃COOH) having a burning taste, sharp odor and pernicious blistering properties.

Nowadays, acetic acid is central to all biological energy pathways, where it can be found in oilfield brines, ocean water and rain. At some concentrations, it is affected in many plant and animal liquids. Fruit and vegetable juices fermentation can be produced about 2–12% acetic acid solutions that named as vinegar. In chemical technology, absorption can be defined as a process in which atoms or molecules transfer from a gas phase into a liquid phase. In addition, there are differences between absorption and adsorption, where absorption the molecules are taken up by a liquid (absorbent, solvent), while for adsorption the molecules are fixed onto solid surfaces. While distillation process is one of the most popular unit operations. In fact, the mechanism of process established on the different boiling points of the materials to split. It is done by mixing two or more components is brought to the boiling point out of many stages of condensation or evaporation tower [9-16].

In this study, the vapor feed stream to the scrubber is a mixture of CO₂, N₂ and acetic acid. Therefore, acetic acid is to be recovered. Experimentally, it is hard to know the effect of different process parameters such as pressure, temperature, flow rate and number of theoretical stages as well as the quality of product. Because of these reasons, the simulation study has been done by investigating and analyzing the process results to optimize techniques to choose the best design to gain acetic acid from the process stream. On the other hand, it should be separated from CO₂. The main aim of this project is to model the production of acetic acid by oxidation of ethylene with Aspen Plus, and sub-objectives can be listed as: To find out and describe of the amounts of produced acetic acid. Simulate the absorption process using ASPEN PLUS. And

find out the effect of various parameters as follows: Pressure, Temperature, Flow rate, and Number of theoretical stages.

Methodology

This study investigates the design and optimization model of acetic acid production by oxidation of ethylene by modeling using Aspen Plus software. The input to simulation process is the vapor feed stream with CO₂, N₂ and acetic acid in specific concentrations, pressure and temperature in scrubber. From other side, fresh water comes from the top of scrubber tower as second input. This research designs a RadFrac absorption unit, which will scrub acetic acid from CO₂ containing stream. RadFrac is known as rigorous model for simulating all multistage vapor liquid fractionation operations. In Aspen Plus, it can be used to simulate absorption process. RadFrac has the advantage where it can be simulating modeling columns with two liquid phases and chemical reactions in each liquid phase occurring simultaneously, using different reaction kinetics for each of the two liquid phases. Moreover, it investigates the effect of various process parameters such as pressure, temperature, flow rate and number of theoretical stages. The results of process have been investigated and analyzed, and finally conclusions and recommendations are presented.

Modeling

1. Production Process

The production model is designed with three stages, all stages have particular functions. Stage one is plug flow reactor, stage two is flash drum and last stage is RadFrac absorption or scrubber unit. Third stage is the main stage in this research. Figure 1 shows process flow diagram.

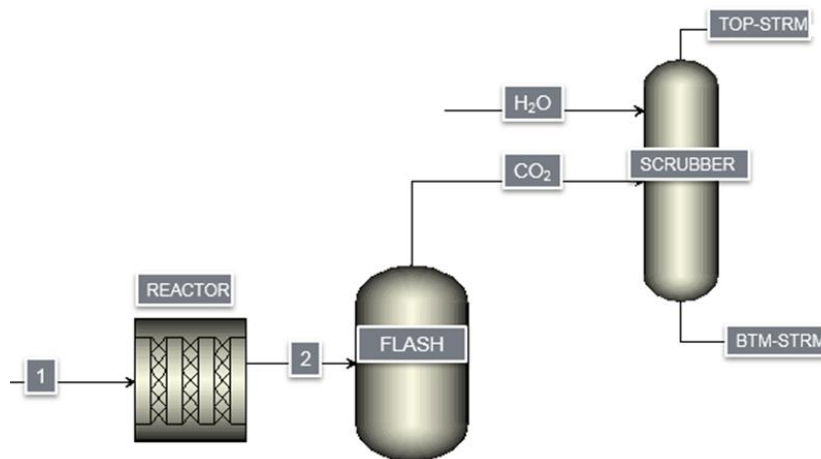


Figure 1: Main flow sheet for the modeling process.

2. PRODUCTION MODEL

• Plug Flow Reactor

Plug flow reactor is first stage in acetic acid production model, in this reactor two reactions have taken place as in Equations 2 and 3. The input to the reactor was air and ethylene; these reacted at a special temperature and pressure, 250 °C and 20 bar respectively, as shown

in Table 1. In addition, the reactor output was used as input in second stage. The plug flow reactor temperature was 250 °C and pressure was 20 bar, where reactor input divided to 30 wt% air and 70 wt% ethylene, while the output contains CH₃COOH with 89.9 wt% which is the highest percentage, CO₂ with 7.2 wt% and the lowest value was H₂O with 2.9 wt%. It should mention that the feedstock to the reactor were air and ethylene where the ratio was 30 wt% air and 70 wt% ethylene. Nitrogen is essential element of air and does not have any effect on the reaction as it known as inert gas. In present equation, the ratio of N is small (traces).



$$\text{Yield Percent} = \frac{\text{theoretical yield of product}}{\text{actual yield of product}} \times 100$$

For first reaction at equation 2:	For second reaction at equation 3:
Theoretical yield = 150	Theoretical yield = 110
Actual yield = 36.31	Actual yield = 36.10
Percent yield = 24.20 %	Percent yield = 32.81%

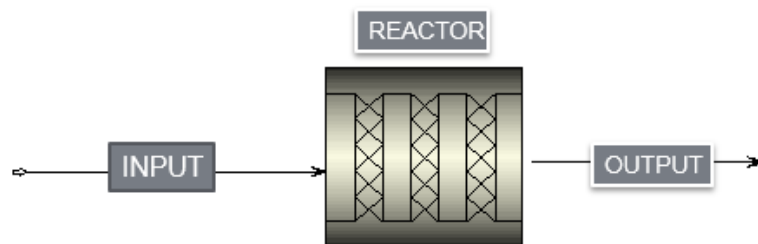


Figure 2: Stage 1, the reactor plugs flow reactor.

Table 1: Stage 1, Plug flow reactor input and output.

TEMPERATURE °C	PRESSURE bar	INPUT wt%		OUTPUT wt%	
250	20	Air	30	CH ₃ COOH	89.9
		Ethylene	70	CO ₂	7.2
				H ₂ O	2.9

• Flash Drum

The second stage is the flash drum, as seen in Figure 3. This stage that utilizes the reactor output as input. More details about input and output are shown in Table 2. CO₂ was produced from this stage used as input in Radfrac absorber to produce acetic acid. The input of flash drum contains the output of plug flow reactor, which are CH₃COOH with 89.9 wt% which is the highest percentage, CO₂ with 7.2 wt% and the lowest value was H₂O with 2.9 wt%, while the flash drum output is divided as CH₃COOH with 0.6 wt%, CO₂ with 98.2 which the highest percentages and N₂ with 1.2 wt%.

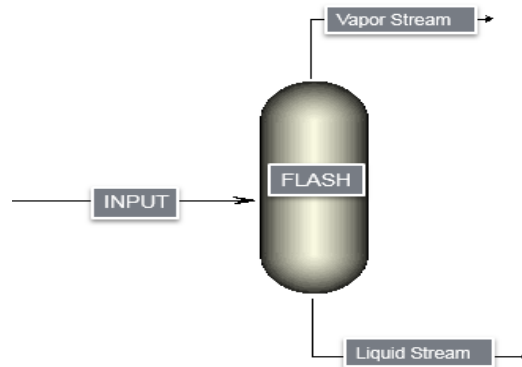


Figure 3: Stage 2, flash Drum.

Regarding to electrochemistry nature of water. The bond O-H can stretch and rise absorption band. The H-O-H bending mode origin is also large. The infrared spectrum of liquid water is dominated by the intense absorption due to the fundamental O-H stretching vibrations. Therefore, this high intensity requires very short path lengths, and the absorption band is broader than might be expected due to hydrogen bonding. Addition to water, the following can be used: carbon tetrachloride, ether, ethyl alcohol and glycerol. However, using (NaOH) which considers as strong base to absorb acetic acid leads to produce sodium cations and hydroxide anions as it is totally dissociated in aqueous solution. Sodium acetate is produced because of this reaction. Similarly, sodium acetate soluble and in turn exist as ions.

Table 2: Stage 2, Flash unit input and output.

INPUT wt%		OUTPUT wt %	
CH ₃ COOH	89.9	CH ₃ COOH	0.6
CO ₂	7.1	CO ₂	98.2
H ₂ O	2.9	N ₂	1.2

- **RadFrac scrubber**

In stage 3, the RadFrac absorption or scrubber unit was designed to produce the largest possible amount of acetic acid. As rigorous model, the RadFrac is useful for to simulating all types of multistage vapor liquid fractionation processes. In fact, it can simulate: Absorption and Stripping. In addition, RadFrac can be utilized with different kinetics for two liquid phases, as well as the model columns with two liquid phases chemical absorption in each liquid phase occurring simultaneously. RadFrac consists of trays used with especial size and rate columns. Moreover, it is the largest and most important stage of equipment in an acetic acid plant. RadFrac can treat large volume of flue gas. In this stage, the absorber column was designed based on equilibrium principles using the model data, which was created by using ASPEN Plus, as shown in Figure 4. Table 3 shows the Radfrac input, CO₂ and H₂O of this unit, where the stage flow rate, temperature and pressure has been shown. All inputs absorbed within 6 stages inside Radfrac. Acetic acid was produced in bottom stream as liquid. The flow rate, temperature and pressure have been controlled and sensitivity analysis was performed as well on the process production.

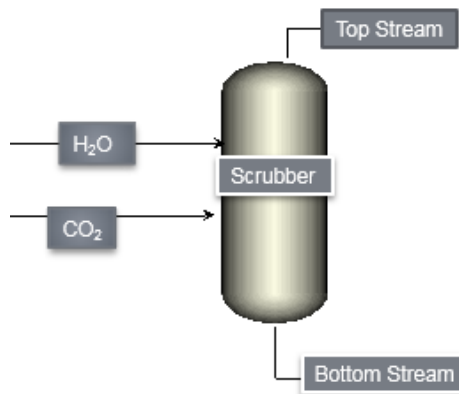


Figure 4: Stage 3, Radfrac scrubber.

Scrubber designed to control gaseous emissions and work on avoiding some unwanted gasses through exhaust streams. In current system water was used, the choice actually depends on the concentration of acetic acid inter the scrubber and somehow on the efficiency of gas removing. In case of low flow where the pollutants release frequently, water scrubber success to eliminate toxin. Moreover, when acetic acid produce at heavier amounts the better instead method is distillation column or a recirculated alkali solution.

Table 3: Stage 3, Radfrac input and output.

	H2O stream		CO ₂ stream	
	INPUT			
FLOW RATE kmol/hr	150		100	
TEMPERATURE °C	25		40	
PRESSURE bar	10		10	
Composition wt%	Water	150	CO ₂	98.2
			CH ₃ COOH	0.6
			N ₂	1.2

Results

1. Production By Scrubber

The main stage of our modeling design is the third stage, which is the RadFrac scrubber unit. This unit has been designed to produce the largest possible amount of acetic acid and produce CO₂ as pure as possible. Moreover, RadFrac represented as the largest and most important stage of equipment in an acetic acid plant. Figure 4 shows the third stage which is the absorber column based on equilibrium principles using the model data in simulation software. Acetic acid has been produced as liquid in the bottom stream using six stages because the absorption factor is high according to liquid feed height inside Radfrac. In addition, the flow rate, temperature and pressure have been controlled and analyzed as sensitivity parameters.

Table 4 shows the mole flow of input and output of the scrubber. CO₂ stream bottom input with 98.2 kmol/hr total mole flow at 40 °C temperature and 10 bar pressure. The top input was H₂O stream with a mole flow of about 150 kmol/hr, at 25 °C temperature and as same as CO₂ stream pressure 10 bar. The basic product is acetic acid, which is produced in the bottom stream

with mole flow about 0.6 Kmol/hr, at 30.3 °C temperature and 10 bar pressure. The aim of this study scrub acetic acid at the Bottom stream. In addition, the separation process is excellent with the highest percentage of acetic acid at the bottom stream. Note that the proportion of CO₂ gas dissolved in water, because it is solved in water while nitrogen gas difficult to dissolve in water, for this reason most of the nitrogen gas flowed up as upper stream.

Table 4: Mole flows for all streams of the scrubber.

		BOTTOM INPUT	TOP INPUT	BOTTOM PRODUCT	TOP PRODUCT
Phase		Mixed	Liquid	Liquid	Vapor
Temperature	°C	40	25	30.3	26.5
Pressure	bar	10	10	10	10
Mole Flows	kmol/hr	100	150	151.078	98.921
CO₂	kmol/hr	98.2	0	0.820	97.379
H₂O	kmol/hr	0	150	149.657	0.342
CH₃COOH	kmol/hr	0.6	0	0.6	1.26 E-14
N₂	kmol/hr	1.20 E+00	0	0.0002	1.199

Table 5 shows the mole flow for RadFrac input and output. The RadFrac bottom input started with CO₂ at 0.982 kmol/hr mole fraction at 40 °C temperature and 10 bar pressure. The top input was H₂O with mole flow about 150 kmol/hr, at 25 °C temperature and 10 bar pressure. The basic product is acetic acid, which is produced as bottom stream with mole fraction of 0.004 at 30.3 °C temperature and 10 bar pressure and some of it as top stream nearly 1.27 E-16 kmol/hr at 26.571°C temperature and 10 bar pressure. In this study, we will recover acetic acid from diluted CO₂ mixture and that it would like to make an almost pure CO₂ in this system. That concluded at top stream CO₂ at high purity. The purity of acetic acid was at the bottom stream is about 0.004 while in the top stream it is zero.

Table 5: The mole fractions for all streams of the scrubber.

		BOTTOM INPUT	TOP INPUT	BOTTOM PRODUCT	TOP PRODUCT
Phase		Mixed	Liquid	Liquid	Vapor
Temperature	°C	40	25	30.3	26.57
Pressure	bar	10	10	10	10
Mole Fractions	kmol/hr				
CO₂	kmol/hr	0.982	0	0.005	0.984
H₂O	kmol/hr	0	1	0.990	0.003
CH₃COOH	kmol/hr	0.006	0	0.004	1.27 E-16
N₂	kmol/hr	0.012	0	1.35 E-06	0.012

The mass flows of all streams are shown in Table 6 for RadFrac input and output. The mass flow of RadFrac bottom input started with CO₂ stream has a flow of 4321.762 kg/hr at 40 °C temperature and 10 bar pressure. The top input was H₂O stream with 2702.292kg/hr flow, 25 °C temperature and as same as CO₂ pressure 10 bar. The acetic acid produces as bottom stream with mass flow about 36.031 kg/hr, at 30.3 °C temperature and 10 bar pressure and some of it leaves as top stream at a rate of 7.57 E-13kg/hr, at 26.5 °C temperature and 10 bar pressure.

Table 6: The mass flows for all streams of the scrubber.

		BOTTOM INPUT	TOP INPUT	BOTTOM PRODUCT	TOP PRODUCT
Phase		Mixed	Liquid	Liquid	Vapor
Temperature	°C	40	25	30.3	26.5
Pressure	bar	10	10	10	10
Mass Flows	kg/hr	4391.410	2702.292	2768.264	4325.438
CO ₂	kg/hr	4321.762	0	36.100	4285.662
H ₂ O	kg/hr	0	2702.292	2696.126	6.165
CH ₃ COOH	kg/hr	36.031	0	36.031	7.57 E-13
N ₂	kg/hr	33.616	0	0.006	33.610

Table 7 shows the mass fraction for RadFrac stream input and output. The RadFrac bottom stream has a rate of CO₂ at 0.984 kg/hr mass flow at 40 °C temperature and 10 bar pressure. The top input was H₂O stream with mass flow about 1 kg/hr, 25 °C temperature and as same as CO₂ pressure 10 bar. The basic product is acetic acid, which produces as bottom stream with mass fraction about 0.013 kmol/hr, at 30.3 °C temperature and 10 bar pressure and some of it as top stream nearly 1.75 E-16 kmol/hr, at 26.5 °C temperature and 10 bar pressure.

Most of the acetic acid produced in the liquid phase, because molecules of the organic acid are non-volatile and interconnected that's why acetic acid gather at the last stage and exit the bottom stream. The tiny amount of CO₂ resulted from conversion of acetic acid and this in turn refer to a small over-oxidation in air stream, and contribute in decrease of acetic acid production. It can overcome this problem by efficient aeration. In addition, by controlling the airflow of feedstock, which reduce air contact with ethylene and lead to prevent undesired gases to be exist. Figure 5 shows the mole fraction for CH₃COOH with respect of every stage in RadFrac.

Table 7: The mass fraction of all streams.

		BOTTOM INPUT	TOP INPUT	BOTTOM PRODUCT	TOP PRODUCT
Phase		Mixed	Liquid	Liquid	Vapor
Temperature	°C	40	25	30.325	26.571
Pressure	bar	10	10	10	10
Mass Fractions	kg/hr				
CO ₂	kg/hr	0.984	0	0.013	0.990
H ₂ O	kg/hr	0	1	0.973	0.001
CH ₃ COOH	kg/hr	0.008	0	0.013	1.75 E-16
N ₂	kg/hr	0.007	0	2.06 E-06	0.007

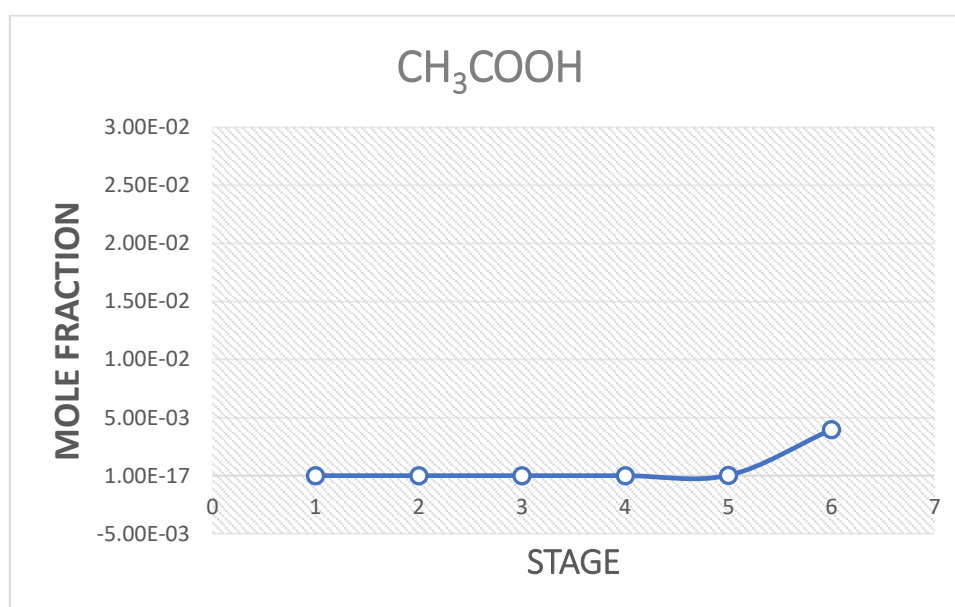


Figure 5: The mole fraction of acetic acid at every stages.

Conclusion

This study aims to design and optimize model of acetic acid production by oxidation of ethylene by modeling using Aspen Plus software and also to understand and study the production process of acetic acid. From the simulation, the main conclusions are drawn as following. Acetic acid has been produced as liquid in bottom stream after six stages inside Radfrac. Moreover, the flow rate, temperature and pressure have been controlled and analyzed as sensitivity parameters. The production capacity according to simulation model was 4599 kmol/hr, which is about 276177.6 kg/hr.

The basic product is acetic acid produced as bottom stream with mole flow about 0.6 kmol/hr, at 30.3 °C temperature and 10 bar pressure. The mole fraction of acetic acid produced as bottom stream is about 0.004 at 30.3 °C temperature and 10 bar pressure. According to the simulation results, the optimum mole fraction of acetic acid reached with stages 6 in RadFrac.

Increasing flow rate of H₂O input stream decreases the mole fraction of CH₃COOH. The highest acetic acid mole fraction was recorded was at start point or lowest flow rate and highest temperature, while there is no effect of pressure. The effects that were shown by CO₂ in production process is much more than that shown by H₂O. Positive relationship indicated, with increasing flow rate of CO₂ input stream increases the mole fraction and mole flow of CH₃COOH as well.

The results shows that increasing temperature of CO₂ input stream the mole flow of CH₃COOH was constant at 0.6 kmol/hr until 165 °C then the CH₃COOH mole flow start decreasing to reach the lowest value at end point, which is 400 °C. Nevertheless, Positive relationship has been noted, with increasing temperature of CO₂ input stream increases the mole fraction of CH₃COOH. The highest acetic acid mole fraction recorded was at end point. The inverse relationship has been realized between total temperature of H₂O input stream and the mole fraction of CO₂. On other hand, the positive relationship has been indicated between total temperature of H₂O input stream and the mole flow of CO₂.

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