Research on Methanol Carbonylation: A Comprehensive Analysis of Acetic Acid Synthesis and Production

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ABSTRACT

Acetic acid, a crucial chemical compound with a wide range of applications across various industries, is predominantly manufactured via the process of methanol carbonylation. The present research delves into the synthesis of acetic acid through methanol carbonylation, with a specific emphasis on the fundamental principles and economic considerations utilizing the PETRO-SIM software. Utilization of this simulation tool facilitated an assessment of the impacts of distinct operational parameters on the yield of acetic acid and the overall distribution of products. The process is bifurcated into two core segments: the first being the reaction unit, wherein methanol and carbon monoxide undergo a reaction within a continuous stirred tank reactor (CSTR), and the other being the separation unit, which encompasses a flash tank and distillation columns. The CSTR is operated at a temperature of 150°C, following which the product stream undergoes a phase separation in the flash tank. Subsequently, the resultant mixture is channeled into the distillation columns for the purpose of segregating methyl acetate, methanol, water, acetic acid, and propionic acid based on their respective boiling points. The simulation was executed employing the SRK (Soave-Redlich-Kwong) property package, taking into account the system's range of moderate to high pressures and low to moderate temperatures. The simulation entailed three distinct reactions, resulting in a production capacity of 23,610 kg/h of acetic acid. The raw materials supplied to the plant were methanol (13,612 kg/h) and CO (12,274 kg/h), as determined by the initial material balance. This investigation imparts significant insights into enhancing the optimization of the acetic acid production process via methanol carbonylation, thereby contributing to the advancement of more effective and sustainable manufacturing methodologies

Keywords: **Acetic Acid, Methanol carbonylation, Rhodium catalyst, Iridium catalyst, Cativa process, Monsanto process, PETRO-SIM simulation, Continuous stirred tank reactor (CSTR, Distillation column**

INTRODUCTION

Acetic acid, also known as methane carboxylic acid or ethanoic acid, is a short-chain saturated fatty acid with a pungent Odor and sour taste.[1] It is vital in producing synthetic fibers, plastics, solvents, inks, and dyes. Increasing global demand for acetic acid is driven by its versatile applications in various chemical processes. Valued at US$ 11.9 billion in 2023, the market is growing due to its use as a feedstock in chemicals like vinyl acetate, acetic anhydride, and acetate esters, alongside significant growth in the chemical industry. The rising use of acetic acid in coatings, greases, polyesters, sealants, and other products across industries such as electronics, automobiles, textiles, and packaging also support market growth. Additionally, its role in producing purified terephthalic acid (PTA) for lightweight and recyclable polyethylene terephthalate (PET) bottles further boosts demand.[1] The automotive industry's increasing use of acetic acid for antifreeze and coolant fluids also drives market expansion. Acetic acid is mainly produced through chemical routes that involve homogeneous and heterogeneous catalytic methods.

Acetic acid can be synthesized through various methods such as hydrocarbon oxidation, anaerobic fermentation, and methanol carbonylation.[2] Methanol carbonylation is the most promising technology for Acetic acid synthesis compared to other methods. Production processes mostly rely on methanol carbonylation catalysed by Rhodium or Iridium compounds.[3] Cativa process introduced in 1996 by BP Chemicals is more efficient and cost-effective for producing high-quality acetic acid with low impurity content.[4] Iridium-based catalysts in methanol carbonylation lead to stability improvements and expanded operating conditions, reducing side reactions and enhancing selectivity. The Cativa process offers a variety of catalysts and process intensification, while the fermentative approach using Acetobacter bacteria for ethanol oxidation is slower and less efficient for industrial-scale production. Despite recent attention, commercial application of the fermentative method is not yet established in acetic acid production. In sustainable manufacturing, there is a growing need to develop more environmentally-friendly routes for acetic acid production.[5]

In 1910s, scientists discovered that acetic acid could be synthesized from methanol and carbon monoxide under extreme conditions of pressures exceeding 100 bar and temperatures above 300°C.[3] Combinations of CO and methanol work under the influence of various metal catalysts. In the 1970s, Monsanto Corporation developed a rhodium complex catalyst for methanol carbonylation, consisting of rhodium complexes and iodide, enabling the reaction under mild conditions at pressures of 3-6 MPa and temperatures of 150-200°C.[3] Efforts to enhance catalyst performance resulted in the rhodium catalyst (Monsanto process) and iridium-based catalyst (Cativa TM process), both operating as homogeneous catalysts with high activity at reduced water concentrations. The Cativa process, being greener and more efficient, has largely replaced the Monsanto process. Nevertheless, the homogeneous catalyst is still used in about 85% methanol carbonylation process.

The majority of the literature concentrates on investigating the influence of the catalyst on the chemical reaction. This academic investigation delves into the intricacies of synthesizing acetic acid through methanol carbonylation, scrutinizing the underlying principles and economic aspects using PETRO-SIM software. The simulation tool was utilized to assess the effects of different operational variables on the yield of acetic acid and the overall distribution of products.

PROCESS DESCRIPTION

The whole plant is segmented into two sections: the reaction unit and the separation unit. The block diagram may be consulted from Fig.1. Methanol carbonylation occurs in a continuous stirred tank reactor (CSTR) with methanol and carbon monoxide as inputs. Due to the exothermic nature of the reaction, the reactor is equipped with an external cooling jacket to maintain a temperature of 220°C (Carbonylation zone is preferably maintained at a temperature in the range of 150 to 220 °C and most preferably in the range of 170 to 220 °C; hence while doing simulation, temperature is maintained at 220 °C) with initial heat provided by steam.[1] The CSTR product stream, rich in acetic acid and containing methanol, carbon monoxide, propionic acid, and water, goes through a throttling valve to a flash tank for vapor-liquid separation. The separated product then enters a distillation column, where vapor pressure governs the separation sequence. Methyl acetate (bp 56.9°C) is removed first, followed by methanol (bp 64.7°C), water (bp 100°C), acetic acid (bp 117.9°C), and propionic acid (bp 141.2°C).[4] The mixture enters column DC-1 (distillation column), yielding mixture of acetic and propionic acids as heavy key component and mixture of water, methanol, ethanol, and methyl acetate as light key component. The heavy key component is fed into column DC-2, producing 99.9 mole % acetic acid as the light key component and 90 mole % propionic acid as the heavy key component.
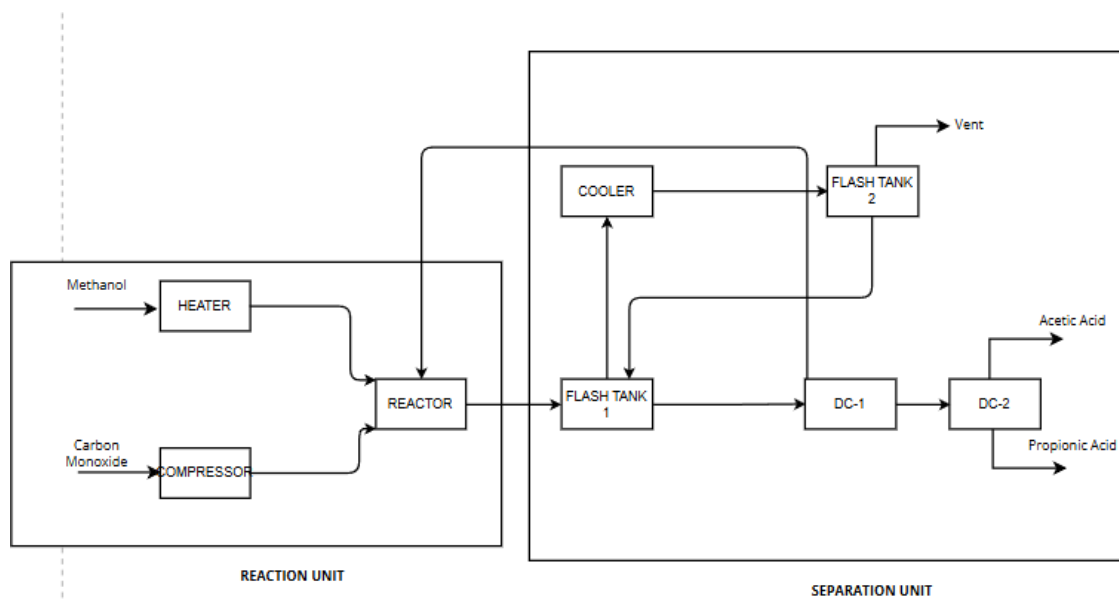

Fig. 1. Block Diagram of the Methanol Carbonylation

1. Simulation of the process by PETRO-SIM

   The simulation of acetic acid production through methanol carbonylation is performed using PETRO-SIM, as illustrated in the process flow diagram provided in the Fig.3. The following assumptions are made while carrying out the simulation:
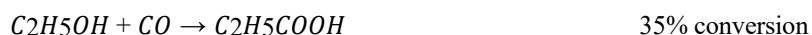
1. The presence of catalysts and promoters is not taken into account in the simulation model
2. The basis for the simulation model is the conversion parameters rather than kinetic parameters
3. The simulation model is formulated as a steady state model
4. The product list in the simulation comprises only molecular species; hence, free radicals and their associated reactions are excluded. The simulation procedure follows the steps outlined below:

List of Components: The components used in this simulation are as following:
a) Methanol
b) Ethanol
c) Carbon Monoxide
d) Acetic acid
e) Propionic acid
f) Methyl acetate
g) Water

Fluid Package: The SRK (Soave-Redlich-Kwong) property package was utilized for the simulations due to the system operating within a range of moderate to high pressures and low to moderate temperatures. This equation of state particularly suitable for accurate predictions in such scenarios. In order to achieve reliable results, the system must be under vapor-liquid equilibrium or liquid-liquid equilibrium conditions, given that the SRK equation of state is specifically tailored for multi-phase equilibrium computations. A similar simulation was conducted using the NRTL Hayden-O'Connell approach by Dimian et al. [4]

Reactions involved: There are three reactions involved in this simulation. Reactions are:

$$CH_3OH + CO \rightarrow CH_3OH \qquad\qquad 95 \text{ \% conversion}$$

$$C_2H_5OH + CO \rightarrow C_2H_5COOH \qquad\qquad 35\% \text{ conversion}$$

$$CH_3OH + CH_3COOH \rightarrow CH_3COOCH_3 + H_2O \qquad 35\% \text{ conversion}$$

Process simulation: Both methanol and carbon monoxide undergo heating and compression by heater and compressor to temperatures of 220°C and 30 bar, respectively, before being introduced into the continuous stirred tank reactor (CSTR). Due to the exothermic nature of the reaction, a cooling jacket is incorporated. The reactor outlet passes through a valve facilitating flash vaporization, followed by the separation of liquid and vapor in the flash tank. To further extract entrained acetic acid from the vapor, another flash tank is utilized. Prior to the recovery process, the stream entering the flash tank is cooled. The vapor released from the second flash tank is vented, while the liquid is returned to the CSTR. The liquid exiting this process is then fed into DC-1.

DC-1, also known as Distillation Column 1, is tasked with the separation of the liquid components. It comprises 35 stages with the feed entering at the 16th stage. This column operates with a reflux ratio of 4.9, primarily aimed at achieving complete water removal. Although a minor quantity of acetic acid is lost in the distillate, it, along with a small amount of methanol, is recycled back to the CSTR. The bottom stream contains propionic acid and acetic acid.
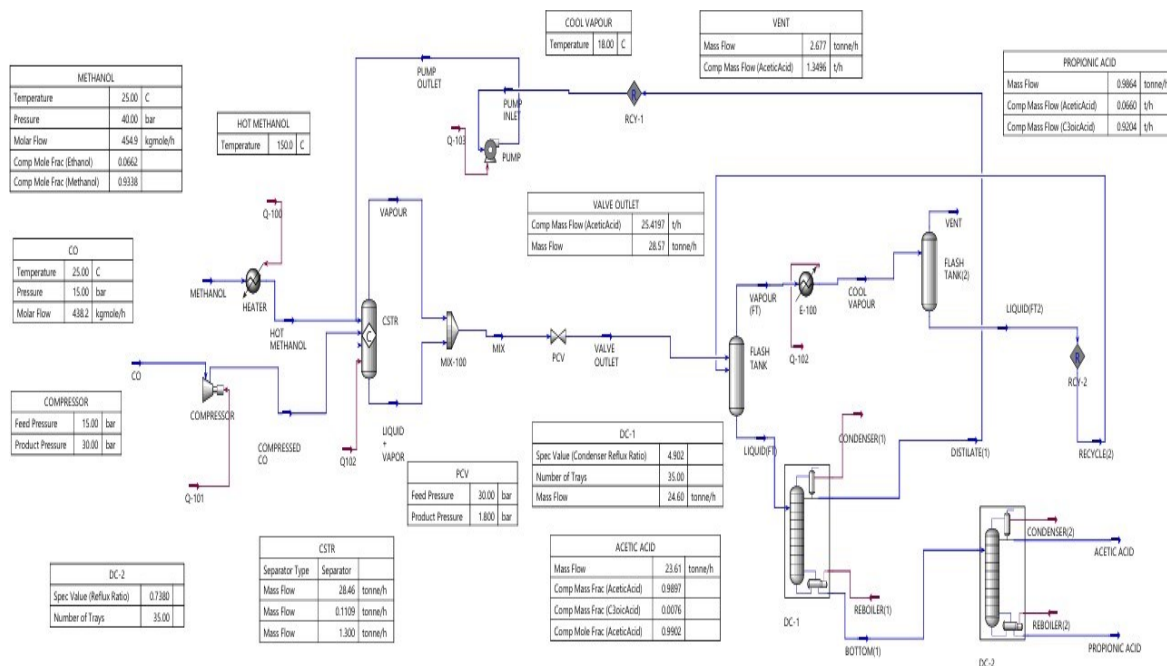
Fig. 2. Process Flow Diagram in simulation

The effluent from the bottom of DC-1 is directed to DC-2, which consists of 35 stages and operates with a reflux ratio of 0.73. The feed is entering at 23rd stage. DC-2's primary function is to separate propionic acid from acetic acid. The distillate yields 23.61 tons/hr of acetic acid, with a residual amount still present in the bottom stream. Propionic acid, on the other hand, is recovered from the bottom with a mass flowrate of 0.92 ton/hr. DC-2 is accountable for the segregation of propionic acid and acetic acid.

There exists a total of 35 stages, excluding the reboiler and condenser, with the 0th and 36th stages representing the condenser and reboiler, respectively. According to the graph, the condenser operates at approximately 120 degrees Celsius, while the reboiler functions at 142 degrees Celsius. Initially, the temperature exhibits a gradual increase; however, after surpassing the 30th stage, a significant temperature rise is observed. The temperature gradient throughout the column can be observed in Fig. 3.
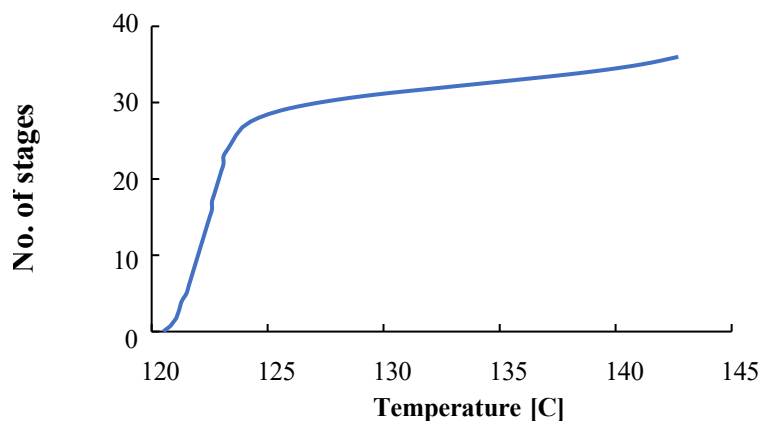

Fig. 3. Temperature gradient across distillation

Certain streams within the system are experiencing acetic acid losses, prompting a detailed analysis to mitigate this issue and enhance process optimization. Through the adjustment of various parameters, the efficiency of the process can be enhanced. Utilizing simulation allows for the identification of the influence of different parameters on the overall process. A more comprehensive delineation of the subsequent analysis will be provided in the following sections.

RESULT AND DISCUSSION

As previously indicated, the model relies on a conversion model; hence, alterations in the reactor parameter may not be conducive for the analysis. As illustrated in Fig. 2 and previously stated, a loss is observed in the separation unit. An analysis is conducted to mitigate this loss and enhance the efficiency of the process. Several parameters are modified to optimize the process efficiency. This will be discussed in depth below.

Feed Entry Stage in DC-2: The feed stage within a distillation column plays a crucial role in the overall distillation process, as it is where the liquid mixture to be separated is introduced into the column. This particular stage is instrumental in determining the efficiency of the distillation process by regulating the temperature within the column through the introduction of the liquid mixture at a specific temperature. The maintenance of proper vapor- liquid equilibrium is of utmost importance in this context. Analysis of the DC-2 aims to enhance its efficiency, with a focus on the fixed specifications in the column, including the distillate rate of 23 ton/hr and the reboiler temperature of 142°C. These specifications aid in upholding consistent process conditions. Simulation-based graphs indicate a decrease in acetic acid concentration when the feed stage is positioned near or at the reboiler, albeit with minimal decrease. Conversely, there is a slight increase in propionic acid concentration observed. The concentrations of both components remain consistent when the feed stage is positioned at or close to the midpoint. Opting for the stage in proximity to the reboiler is favoured for enhanced concentration
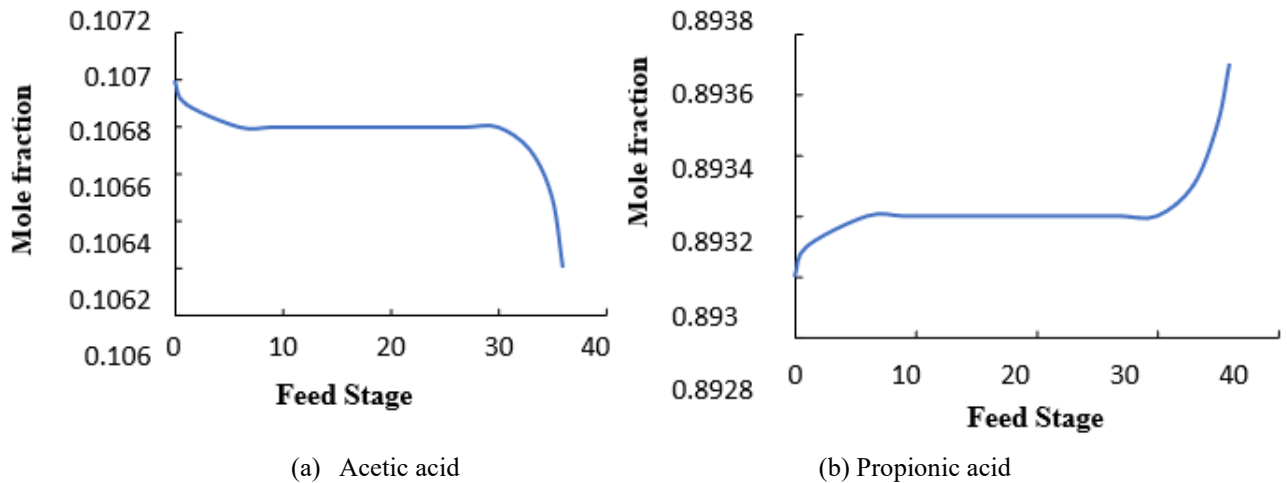

(a) Acetic acid   (b) Propionic acid

Fig. 4. Effects of Feed Stage on product distribution

Reflux Ratio: The reflux ration, a critical factor in the functioning of a distillation column, exerts a notable influence on the composition at the column's base. This ratio, specifically, represents the proportion of liquid reintroduced to the column (reflux) in relation to the liquid extracted from the column (distillate). The efficiency of the distillation column's separation process is impacted by the reflux ratio. An elevated reflux ratio leads to an increased liquid flow back into the column, thereby augmenting the liquid retention and the duration the vapor-liquid mixture remains within the column. Consequently, this heightened reflux facilitates enhanced separation of the feed mixture components by providing more opportunities for these components to interact and segregate based on their respective boiling point.

The composition at the bottom of the distillation column is significantly swayed by the reflux ratio. A higher reflux ratio typically results in a higher purity of the bottom product, as more of the high boiling components are retained in the column and do not make it into the product stream. Conversely, a lower reflux ratio can lead to a lower purity of the bottom product, as more of the high boiling components are carried over into the distillate. From the Fig. 5 the rise in reflux concentration amplifies the presence of propionic acid while diminishing that of acetic acid. Nonetheless, a higher reflux ratio can escalate energy consumption and operational expenses, given the increased energy demand for component separation in the distillate. Therefore, a preferred reflux ratio falls within the range of 3 to 3.5.
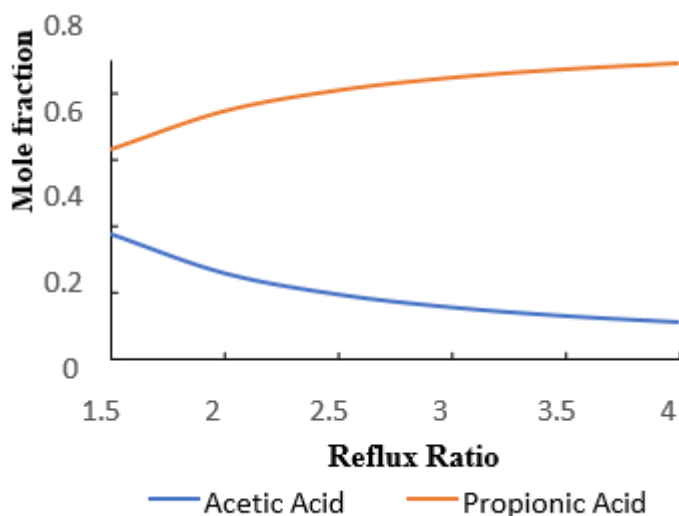
Fig. 5. Effects of Reflux Ratio on product distribution

Reboiler Temperature: The temperature of the reboiler plays a pivotal role in the distillation process, exerting a direct influence on the bottom composition of the distillation column. It is the reboilers responsibility to furnish the requisite heat for vaporizing the liquid feed at the bottom of the column, thereby facilitating the segregation of components based on their respective boiling points.

Typically, the reboiler temperature is calibrated to a specific degree to ensure an optimal efficiency of separation and the desired purity of the end product. Inadequate heating due to a low reboiler temperature may lead to insufficient vaporization of the liquid feed, resulting in subpar separation and decreased product purity. Conversely, an excessively high reboiler temperature can induce thermal degradation of the components, thereby compromising the quality of the final product. With the rise in temperature, there is a decline in the mole fraction of acetic acid and a corresponding increase in the mole fraction of propionic acid at the bottom of the distillation column. It has been noted that higher temperatures may contribute to thermal degradation of the components and escalate energy consumption. This underscores the preference for a reboiler temperature ranging between 142 to 144 degrees Celsious.
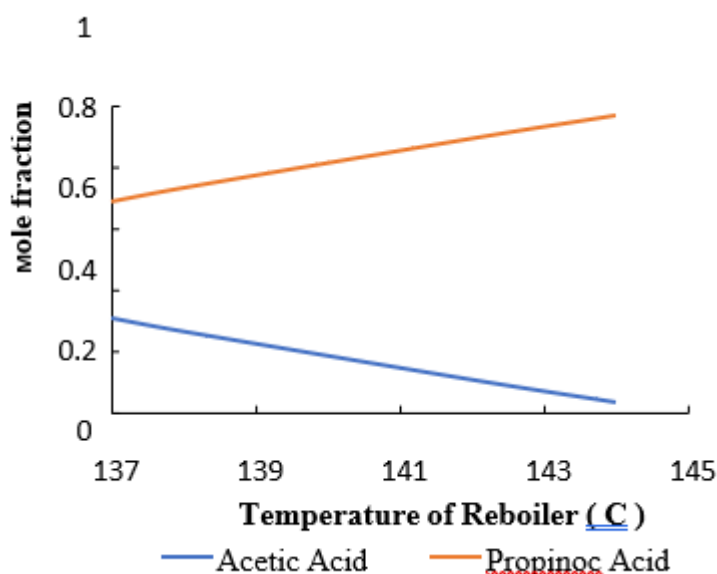

Fig. 6. Effects of Reboiler Temperature on product distribution

Temperature of the Cooler: From Fig. 1, it can be observed that the vapor originating from flash tank 1 undergoes a passage through the cooler, where the stream experiences a cooling effect leading to the condensation of acetic acid into a liquid state, subsequently undergoing separation in flash tank 2. The initial quantity of acetic acid present is recorded at 14.66 tons per hour, and by manipulating the temperature within the cooler, it becomes feasible to induce condensation of the acetic acid, facilitating its collection from the lower section of the second flash tank. Through the utilization of simulations, a comprehensive comprehension of this phenomenon was achieved. The gradual reduction in temperature resulted in an increased yield of acetic acid. The lower temperature of approximately 20 degrees Celsius is more optimal for the process of separation.

However it is imperative to acknowledge the significant energy dissipation accompanying this process. Consequently, the implementation of a heat exchanger network stands as a viable solution for the recovery of the dissipated heat energy.
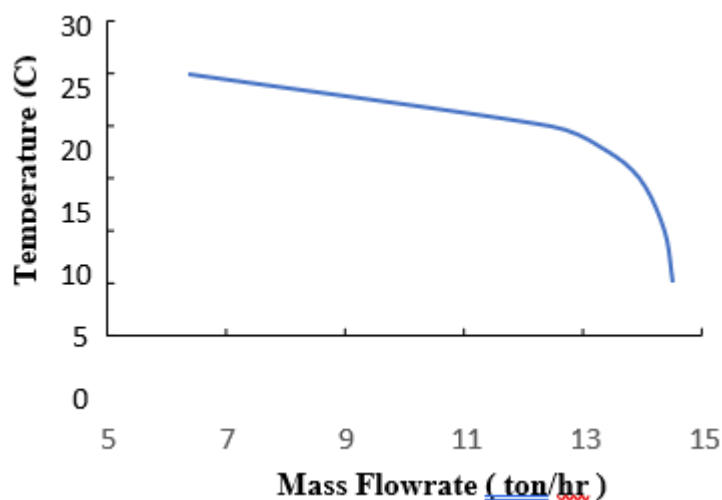

Fig. 7. Effects of Temperature of Cooler on product distribution

CONCLUSION

The study at hand presents the meticulously developed and meticulously simulated process model of a methyl carbonylation process using the software tool PETROSIM. Through the utilization of simulation techniques, a highly successful model was meticulously crafted, and meticulous observations were made regarding the impacts of various parameters. Owing to the unavailability of empirical kinetic data, an intricate conversion model was meticulously formulated. Subsequent to the development of the model, a discernible phenomenon of acetic acid loss in the DC-2 from the base of the column was meticulously observed. Various parameters were meticulously adjusted in an effort to mitigate this loss and meticulous records were maintained of these adjustments.

The meticulous analysis of the impact of crucial process parameters such as cooler temperature, reflux ratio, reboiler temperature, and feed stage was meticulously conducted. Remarkable discoveries arising from the meticulous sensitivity analysis suggest the following key points of interest:

1. The selection of a stage in close proximity to the reboiler is highly recommended for the purpose of augmenting concentration levels.
2. An optimal reflux ratio typically falls within the meticulous range of 3 to 3.5
3. This highlights the significance of opting for a reboiler temperature that falls within the meticulous range of 142 to 144 degrees Celsius.
4. The lower temperature of around 20 degrees Celsius is deemed more optimal for the meticulous process of separation.

    The demonstrated capability of the model in predicting the meticulous optimal conditions for the process is of significant importance, potentially influencing subsequent decisions. The methodology employed for the meticulous modelling and simulation, as exemplified in this research endeavor, is readily comprehensible and reproducible for forthcoming dynamic simulation processes.

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