Production of Formic acid from Methanol

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Background & Process Description:

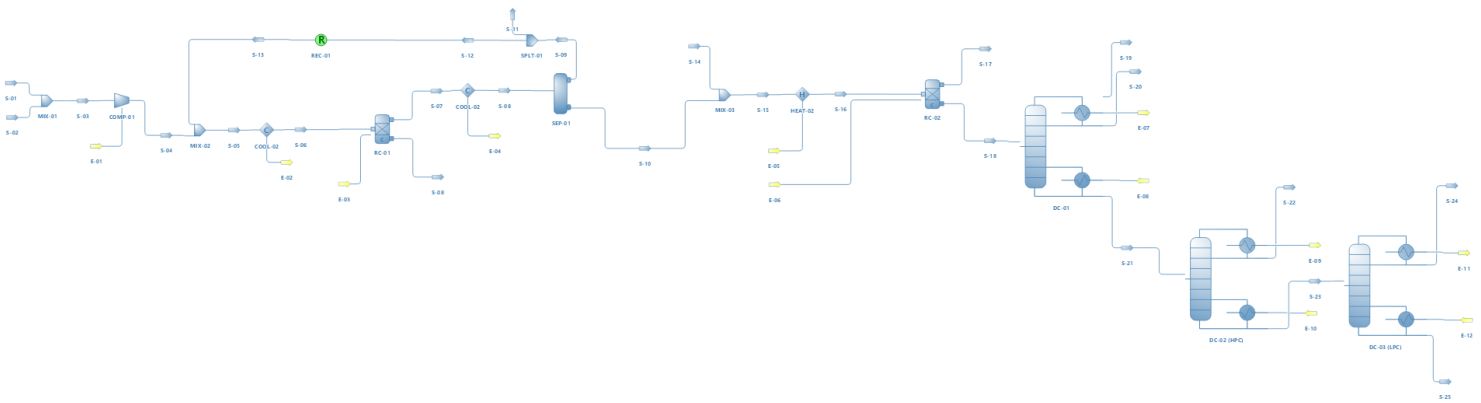
$$CH_3OH + CO \rightarrow HCO_2CH_3 \quad [1]$$

$$HCO_2CH_3 + H_2O \rightarrow HCOOH + CH_3OH \quad [2]$$

Formic acid (methanoic acid) is the simplest carboxylic acid and has a wide range of uses in textile processing, as a preservative, as an antibacterial agent in livestock feed and for cleaning as a substitute for mineral acids. Formic acid is commonly produced by the methyl formate process, using methanol and carbon monoxide as the starting chemicals. First, methanol at 343 K and 1 atm in gaseous state is mixed with the carbon monoxide at STP in the ratio of 1:3.2 , the mixed stream is then compressed to a pressure of 45 bar and is cooled to 363.9 K using a recycling stream at 303 K. The stream is then further cooled to 353 K using a cooler and is then fed to an isothermal reactor where methanol and carbon monoxide react to form methyl formate with a 95% carbon monoxide conversion as shown in reaction 1. The gaseous product stream is then cooled to 303 K and flashed into a vapor-liquid separation drum where the carbon monoxide and other light components are recycled from the overhead stream. Water is then added to the bottom product, which predominantly contains methyl formate, in a ratio of 5:1, since the hydrolysis of methyl formate requires a large excess of water. This stream is then brought to 9 bars and heated to 393 K. The heated stream is fed to another isothermal reactor where water and methyl formate react to form formic acid and methanol with 95% conversion of methyl formate as shown in reaction 2. The liquid product stream is then fed to a distillation column where it is stripped of most of the methanol and other impurities. This methanol can be recycled from the top of the column at the start of the process. A mixture of water and formic acid is obtained from the bottom of the column, since water and methanoic acid form an azeotropic, pressure swing distillation (PSD) is used to break the azeotrope. The stream from the first distillation column is sent to a high-pressure column at 9 bars where mostly water is recovered from the top stream and the bottom stream containing 89% methanoic acid. To further purify this stream, the bottom stream is then fed to a low-pressure column operating at 5 bar pressure. The bottom stream of this column purified 98% formic acid and the top product contained a mixture of water and formic acid which can be recycled.

Thermodynamic property model: UNIFAC

Flowsheet:



Results:

Object	S-25	S-23	S-21	S-18	S-10	S-07	
Temperature	437.335	463.277	445.363	393.15	303.15	353.15	K
Pressure	510000	920000	910000	900000	4.5E+06	4.5E+06	Pa
Mass Flow	0.00981107	0.0103851	0.0311176	0.0395061	0.0158017	0.375674	Kg/s
Molar Flow	0.215755	0.241302	1.31386	1.57899	0.263198	12.7749	mol/s
Molar Fraction (mixture) / Methanol	0	8.69E-21	0.0266099	0.158279	7.57E-11	3.12E-12	
Molar Fraction (mixture) / Carbon monoxide	0	5.99E-151	3.87E-31	7.754E-05	0.000465199	0.956395	
Molar Fraction (mixture) / Methyl formate	1.181E-58	9.488E-40	1.408E-08	0.00833049	0.999535	0.0436047	
Molar Fraction (mixture) / Water	0.0197152	0.106659	0.784329	0.675033	0	0	
Molar Fraction (mixture) / Methanoic acid	0.980285	0.893341	0.189061	0.158279	0	0	

Object	DC-01	DC-02 (HPC)	DC-03 (LPC)	
Pressure	890000	900000	500000	pa
Number of stages	14	73	40	
Feed stage	6	48	14	

Conclusion:

It has been found that three distillation columns of gradually decreasing pressure have proven effective in separating the product from the second reactor. The first distillation column (DC-01) produces a mixture of vapor and liquid as distillate, which consists mainly of methanol. The bottom product of (DC-01) is fed to (DC-02 (HPC)) at 9 bar and then (DC-03 (LPC)), the pressure of 5 bar has been found to be effective in LPC using VLE data in the separation of formic acid with Water.

Reference:

Juan D. Medrano-García, Rubén Ruiz-Femenia, José A. Caballero., “Multi-objective Optimization of a Carbon Dioxide Utilization Superstructure for the Synthesis of Formic and Acetic Acid” Proceedings of the 28th European Symposium on Computer Aided Process Engineering June 10 to 13, 2018, Graz, Austria.