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IIT Jodhpur

Process Development on Aspen

Design Credit Course (Semester 2 of AY 2023-2024)

Under the guidance of Dr Sumit Kamal

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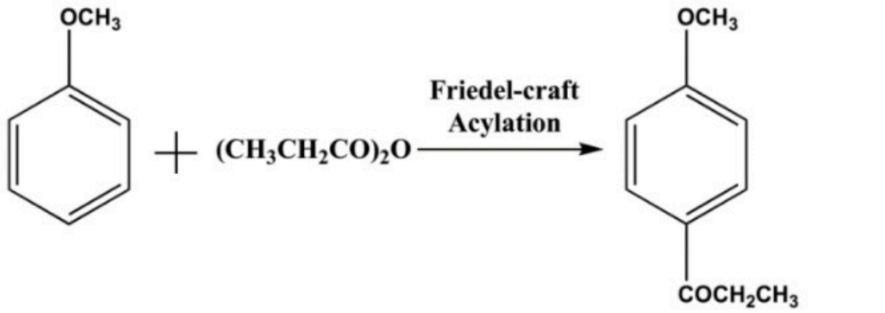
Friedel Craft Acylation reaction of Anisole with Propionic anhydride



4- Methoxypropiophenone are usually prepared by the acylation of anisole with propionyl chloride using $AlCl_3$ as catalyst. $ZnCl_2$, $FeCl_3$, H_3PO_4, and $CoCl_2$ have been reported as catalysts in the liquid phase propionylation of anisole.

Importance of Methoxypropiophenone:

- Methoxypropiophenone are found to have wide applications in the area of fine chemical synthesis.
- 4-Methoxypropiophenone is an intermediate for the production of anethole, which is widely used in preparation of perfumes and flavors.
- It is also used for the synthesis of secoverine, a spasmolytic agent with specific antimuscarinic properties.

KINETIC MODEL:

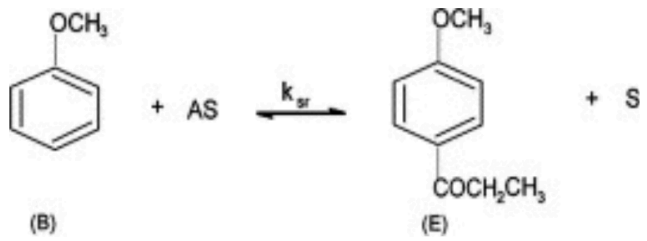
The reaction involves two organic phase reactants, A (propionic anhydride), B (anisole), the desired product E (4-methoxy propiophenone) and C (co-product propionic acid). Since A and B are liquid phase reactants, they need to diffuse to the interior surface of the catalyst. The different steps involved in this process are according to the Eley–Rideal mechanism

Species A (propionic anhydride) gets adsorbed on the active site (S):

$$\underset{\text{A}}{(CH_3CH_2CO)_2O} + \underset{\text{S}}{H^+} \overset{K_a}{\rightleftarrows} \underset{\text{AS}}{CH_3CH_2C^+O} + \underset{\text{C}}{CH_3CH_2COOH}$$

where K_a is the adsorption equilibrium constant.

Now the reaction between the adsorbed A as AS and the liquid phase reactant B (anisole) takes place as follows:



where k_{sr} is the reaction rate constant.

The rate of reaction of B per unit liquid volume (mol/cm$_3$ s) is given by

$$\frac{-dC_{AS}}{dt} = k_{sr} C_B C_{AS} \tag{3}$$

After substituting for C_{AS}, Eq. (3) becomes,

$$\frac{-dC_{AS}}{dt} = k_{sr} K_a C_B C_A C_S / C_C \tag{4}$$

The total site balance is given by

$$C_{total} = w = C_{AS} + C_S \tag{5}$$

where C_{total} or w is the catalyst loading in g/cm^3, and C_S is the concentration of vacant sites.

Eq. (4) can be rewritten with the help of Eq. (5), and suitably manipulated to arrive at:

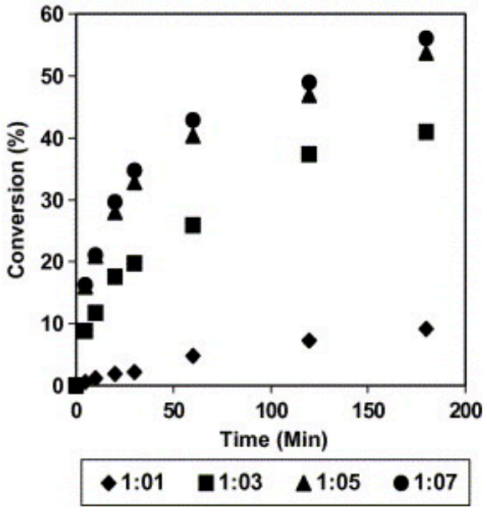
$$\frac{w}{-r_{AS}} = \frac{C_C}{k_{sr} K_a C_A C_B} + \frac{1}{k_{sr} C_B} \tag{6}$$

This can rearrange as follows:

$$\frac{wC_B}{-r_{AS}} = \frac{C_C}{k_{sr} K_a C_A} + \frac{1}{k_{sr}} \tag{7}$$

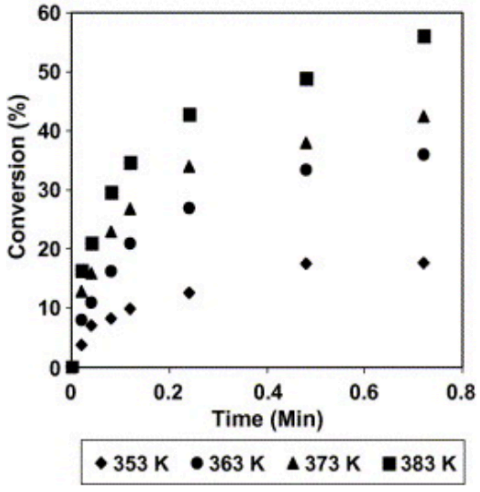
Effect of mole ratio

The effect of propionic anhydride to anisole mole ratio was studied at 1:1, 1:3, 1:5 and 1:7 by keeping the catalyst loading constant. The conversion of propionic anhydride was found to increase with an increase in concentration of anisole. Therefore, all reactions were studied by using a propionic anhydride: anisole mole ratio of 1:5.



Effect of temperature

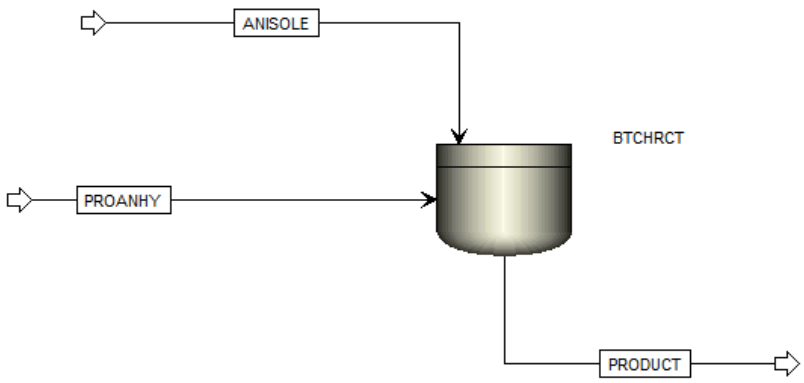
The effect of temperature on conversion was studied under otherwise similar conditions at 353, 363, 373 and 383 K, respectively. It was observed that the conversion increased with temperature. This would suggest a kinetically controlled mechanism.



Batch Reaction:

Batch reactor : A reactor in which the reactants are added to the reactor at the start of the reaction. The reactants are allowed to react in the reactor for a fixed time. No feed is added or product withdrawn during this time. The reaction products are removed at the end of the batch.

Reaction is done in a batch reactor to form 4 Methoxypropiophenone and propionic acid where Anisole is batch feed and propionic anhydride continuous feed.



Method : NRTL RK METHOD

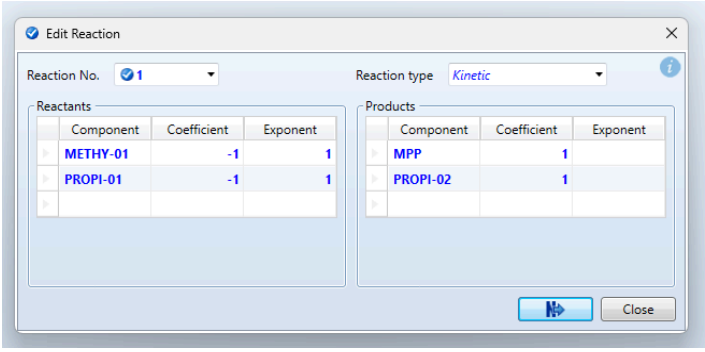
Feed conditions of both Anisole and Propionic Anhydride.

- Pressure: 1 bar
- Vapor Fraction: 0
- Flow rate: 10 Kmol/hr

Batch reactor conditions and specifications:

- Temperature: 75 deg Celsius
- Reactor pressure: 1 atm
- Catalyst loading: 0.5 Kg
- Batch feed time: 1 hour
- Maximum calculation time: 1.5 Hour
- Stop Value: 1.5 Hour

Reaction kinetics:



Reaction type: Kinetic

Reaction: Anisole + Propionic Anhydride → 4-Methoxypropiophenone + Propionic Acid

Reacting phase: Liquid

Kinetic factor = K T^n exp(-E/RT), K = 7.098 x 10^ -5 , n = 0, E=11450 J/kmol

Results:

- Block calculations were completed normally.
- Property calculations were completed normally

Reactor Molar Composition:

Composition profiles

View Reactor molar composition

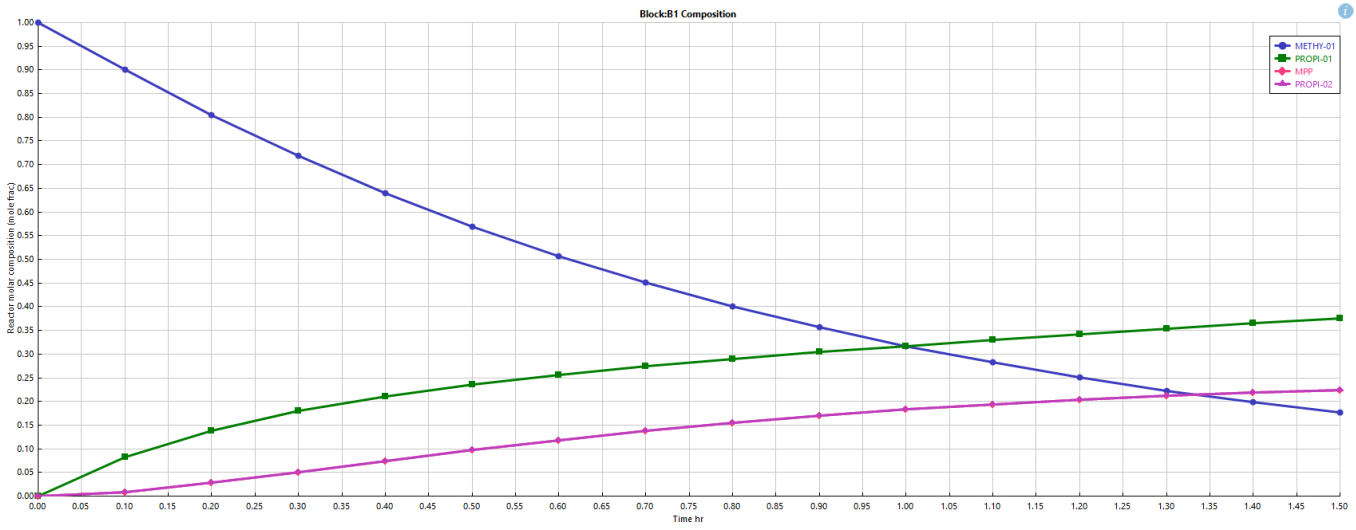
Time hr	METHY-01	PROPI-01	MPP	PROPI-02
0	1	0	0	0
0.1	0.900387	0.0822052	0.0087039	0.0087039
0.2	0.805494	0.138827	0.0278395	0.0278395
0.3	0.718314	0.179853	0.0509164	0.0509164
0.4	0.639607	0.211035	0.0746792	0.0746792
0.5	0.569153	0.23582	0.0975136	0.0975136
0.6	0.506354	0.256354	0.118646	0.118646
0.7	0.450475	0.274005	0.13776	0.13776
0.8	0.400776	0.289665	0.154779	0.154779
0.9	0.356563	0.303931	0.169753	0.169753
1	0.317207	0.317207	0.182793	0.182793
1.1	0.282151	0.32977	0.19404	0.19404
1.2	0.250905	0.341814	0.20364	0.20364
1.3	0.223041	0.353475	0.211742	0.211742
1.4	0.198181	0.364848	0.218485	0.218485
1.5	0.175997	0.375997	0.224003	0.224003

Stream Results:

	Units	ANISOLE	PROANHY	PRODUCT
− Mole Flows	**kmol/hr**	**10**	**10**	**16.6667**
METHY-01	kmol/hr	10	0	2.93328
PROPI-01	kmol/hr	0	10	6.26662
MPP	kmol/hr	0	0	3.73338
PROPI-02	kmol/hr	0	0	3.73338
− Mole Fractions				
METHY-01		1	0	0.175997
PROPI-01		0	1	0.375997
MPP		0	0	0.224003
PROPI-02		0	0	0.224003
− Mass Flows	**kg/hr**	**1081.4**	**1301.44**	**2022.37**
METHY-01	kg/hr	1081.4	0	317.205
PROPI-01	kg/hr	0	1301.44	815.56
MPP	kg/hr	0	0	613.037
PROPI-02	kg/hr	0	0	276.567
− Mass Fractions				
METHY-01		1	0	0.156848
PROPI-01		0	1	0.40327
MPP		0	0	0.303128
PROPI-02		0	0	0.136754
Volume Flow	l/min	20.8799	25.5971	33.6442

Conversion: 37.33%

Graph:



Distillation:

It is the process of separating the components of a liquid mixture through selective evaporation and condensation. The basis of separation is the difference in the vapor pressures (volatilities) of the respective components.

Batch distillation refers to the use of in batches, meaning that a mixture is distilled to separate it into its component fractions before the distillation still is again charged with more mixture and the process is repeated. It is an important part of the production of seasonal or low capacity and high purity chemicals. It is a very frequent separation process in the pharmaceutical industry.

Modeling and simulation of batch distillation on Aspen Plus:

We have a reaction mixture of 4 components that is **Anisole, propionic anhydride, 4-Methoxypropiophenone and propionic acid** which we now want to separate using batch distillation.

Boiling points are:

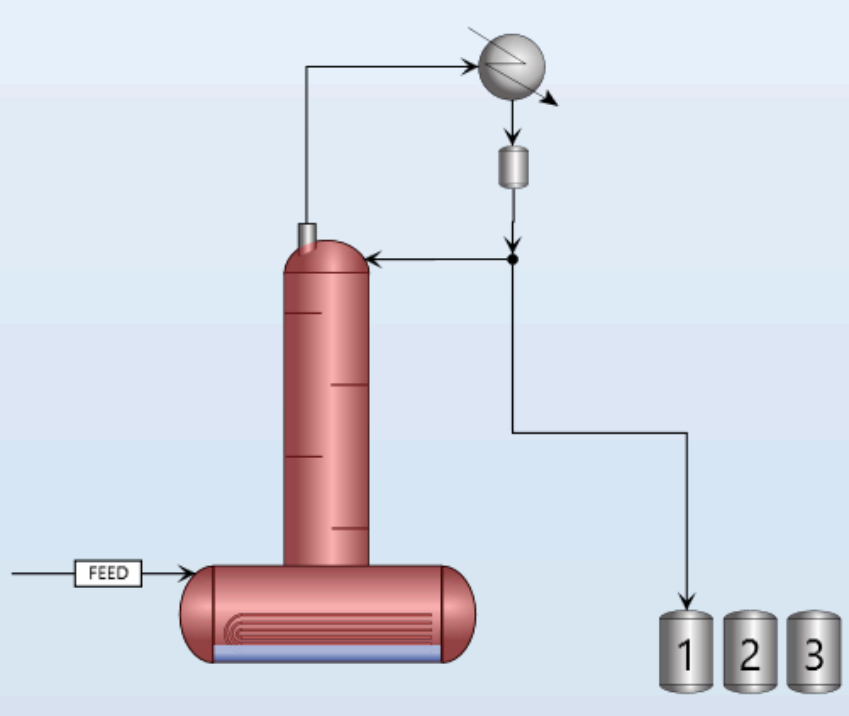
- Anisole: 154 deg Celcius
- Propionic Anhydride: 167 deg Celcius
- 4-Methoxypropiophenone: 243deg Celcius
- propionic acid: 141 deg Celcius.

Propionic Acid is the most volatile among the four as it has the lowest boiling point so firstly it will vaporize and will be collected in the first distillate liquid receiver.

Anisole is the second most volatile among the four and it will start to vaporize after propionic acid as the temperature will increase with time and it will be collected in the second distillate liquid receiver.

Propionic Anhydride in the third receiver.

4-Methoxypropiophenone will be left in the reactor and can be taken out.



Method : UNIFAC

Feed conditions are:

- Feed contains the reaction mixture.
- Temperature: 25 deg Celcius
- Pressure: 1 atm
- Total Flow rate: 10 kg/min
- Mass Fraction of each component is: 0.25

Batch conditions and specifications:

- Number of stages: 25
- Number of receiver: 3
- Initial condition: Total reflux
- Condenser pressure: 15 atm
- Column Pressure Drop: 0.0986923 atm
- Stage holdup: 0.005 Kg
- Condenser: Total
- Geometry specification of reactor: Horizontal
- Volume: 10L
- Diameter: 20 cm
- Heat transfer specific duty: 1.4 kW
- Total initial charge: 8 Kg

Column internals:

- Start stage: 2
- End Stage: 24
- Internal Type: Trayed
- Tray spacing 14.5 cm
- Diameter: 10 cm

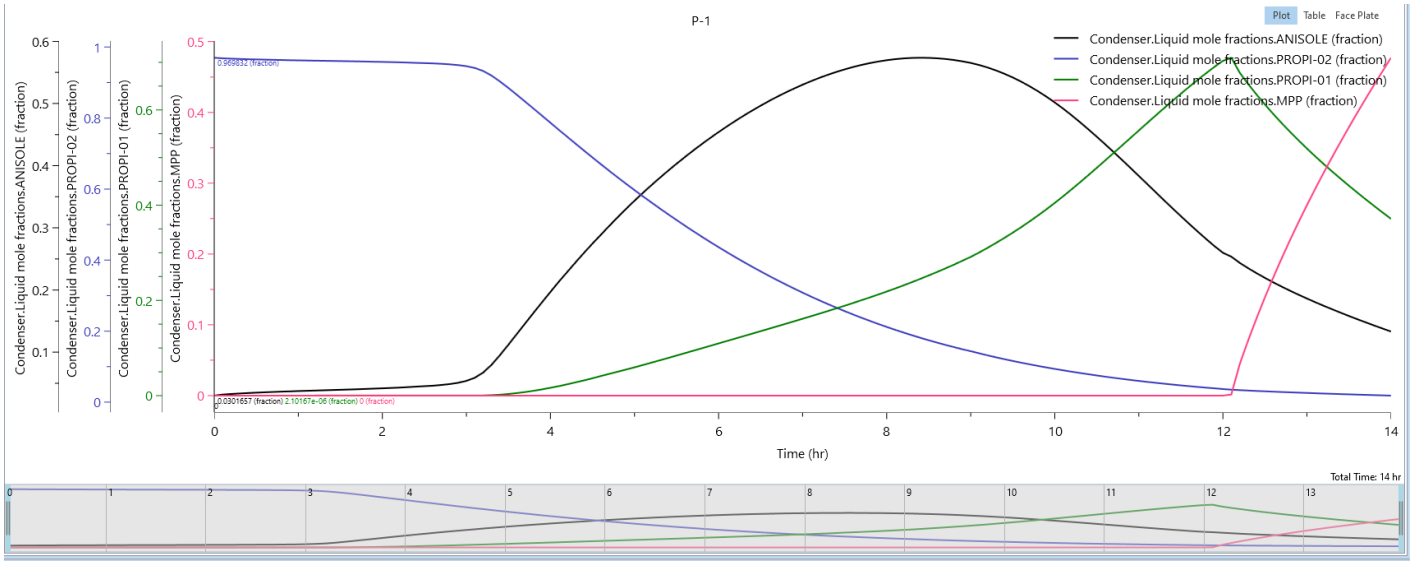
Operating steps:

- Reflux ratio: 40
- Total duration of reaction: 14 Hours
- Duration of 1st liquid distillate receiver: 4.5 hours
- Duration of 2nd liquid distillate receiver: 6 hours
- Duration of 3rd liquid distillate receiver: 3.5 hours

Results:

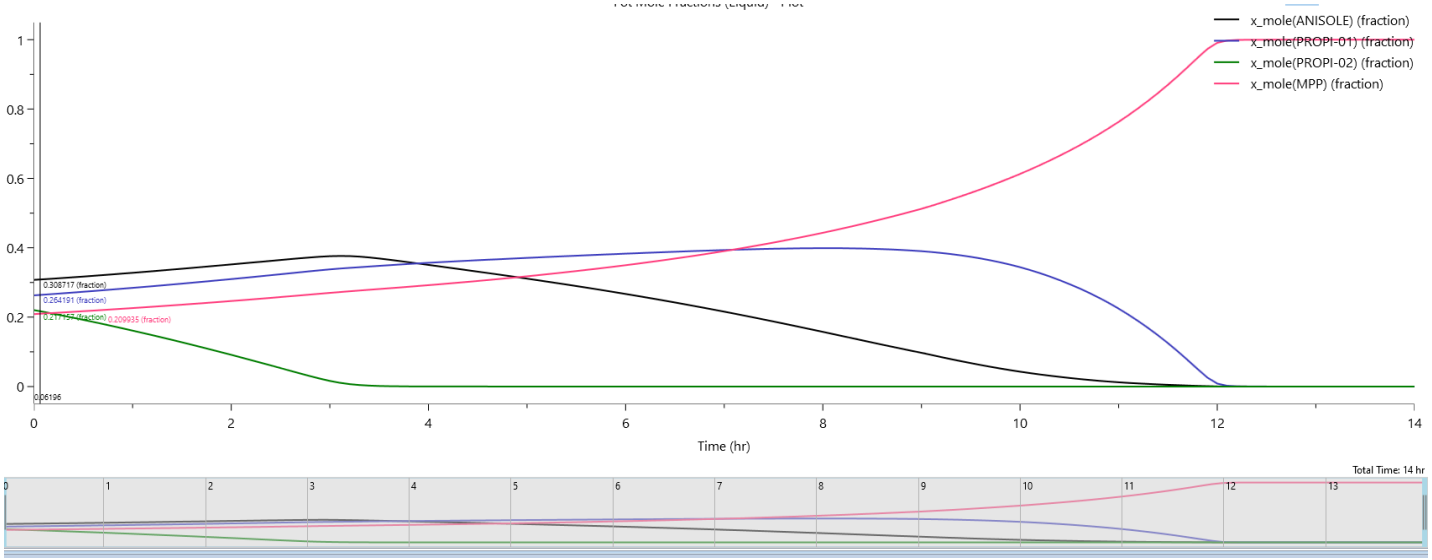
Block calculations were completed normally

Property calculations were completed normally



Condenser liquid mole fraction vs Time.

The concentration of propionic acid firstly increases then decreases. Then the concentration of anisole increases and then decreases. Then the concentration of propionic anhydride increases in the condenser. By this method, we can separate the compounds.



Reactor mole fraction vs time

As the three volatile compounds vapourizes, their concentration decreases with the time in the reactor

4-Methoxypropiophenone is left almost alone in the reactor which can be further used in the production of Anethole.

Recommendations:

1. Increasing pressure of the condenser helps in better separation by increasing the difference in boiling point of components of nearly the same volatility.
2. Increase in stages helps in better separation of compounds.
3. Increase in reflux ratio increases the amount of liquid on the trays which helps to improve the separation of the components. But, increasing reflux ratio reduces the amount of product that is withdrawn from the column.