Steady State Simulation of a Novel Process for the Co-production of Vinyl Acetate and Acetic Acid

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Abstract: A new process for the co-production of vinyl acetate monomer and acetic acid from ethane feedstock was studied. Various configurations were proposed and simulation results were given for each case to optimize process variables. This new process offers an overall yield values above 70% with minimum separation steps involved and the possibility of utilities integration. The process does not involve any CO production, thus becoming environmentally more favorable. The initial capital investment of the proposed process is much lower compared to the conventional route.

Key words: Vinyl acetate, acetic acid, ethane, ethylene.

1. Introduction

Vinyl acetate monomer (VAM) is a chemical building block used to manufacture a wide variety of downstream useful products. It is mainly used for the production of polymers and copolymers used in the production of paints, adhesives and textiles. It was firstly produced via the catalytic reaction between acetic acid and acetaldehyde. This process was developed in Munich by Consortium F. Elektrochemische and further developed by Wacker Chemie in Burghausen. A new process for VAM production was developed by Celanese Corporation of America involving the catalytic reaction of acetic anhydride with acetaldehyde to form ethylidene diacetate which is subsequently decomposes to VAM and acetic acid. Until 1965, almost all VAM was produced using acetylene process and only two smaller plants used the ethylidene diacetate process. Recently, the most widely used process for VAM production involves the catalytic reaction of ethylene and acetic acid with oxygen. This process was commercially used for VAM production since 1968. It can be carried out in either liquid or gaseous phase but according to corrosion problems and formation of by products, the former process is no longer used [1, 2]. In order to produce VAM, acetic acid feed stock should be available. Acetic acid was firstly produced via acetaldehyde oxidation process since 1916. In the period of 1950-1960, new technologies for acetic acid production involving oxidation of hydrocarbons (n-butane, naphtha) were appeared. At the same time, acetic acid production via methanol carbonylation was developed. It was firstly commercialized by BASF in 1960 and further improved by Monsanto in 1970. In 1997, direct oxidation of ethylene for acetic acid production was developed and commercialized by Showa Denko. Approximately, 60% of the world production of acetic acid employs the methanol carbonylation process (Monsanto process) [3, 4].

It is obvious that the nature of the raw materials results in the need of two separate upstream plants, with a cracker. The presence of this petrochemical complex results in large investments to achieve the feasibility of VAM production.
The proposed catalytic process was suggested to overcome this problem and co-produce VAM and acetic acid via ethane feed stock. Using ethane instead of ethylene as a feed stock has the advantage of being available in natural gas so, it is much cheaper than ethylene [5, 6]. The process involves two steps: In the first step, a mixed metal-oxide catalyst, which is commercially available in different compositions, is used in partial oxidation reaction to convert ethane to both ethylene and acetic acid [7]. Various compositions of this catalyst are available resulting in controlled ratios of ethylene to acetic acid. In the second step, the reaction mixture is further oxidized to VAM in the presence of the conventional VAM catalyst. Depending on the ratio of products from the first reaction step, the process allows the co-production of acetic acid. Various configurations were proposed and simulation results were given for each case to optimize process variables.

2. Process Description

The proposed process is composed of two basic sections. The first one involves the catalytic co-production of acetic acid and ethylene from ethane and oxygen using mixed metal oxide catalyst. Reactions taking place on the catalyst surface are believed to be:

\[ \text{C}_2\text{H}_6 + 0.5 \text{ O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]  
\[ \text{C}_2\text{H}_4 + \text{O}_2 \rightarrow \text{CH}_3\text{COOH} \]  

(1) 
(2)

Ethylene undergoes a deep oxidation reaction producing carbon dioxide:

\[ \text{C}_2\text{H}_4 + 3 \text{ O}_2 \rightarrow 2\text{CO}_2 + 2 \text{H}_2\text{O} \]  

(3)

The second section of the process involves the catalytic conversion of ethylene and acetic acid, in the presence of oxygen, to VAM using Pd/Au conventional catalyst according to the following reaction:

\[ \text{C}_2\text{H}_4 + \text{CH}_3\text{COOH} + 0.5 \text{ O}_2 \rightarrow \text{CH}_2\text{CHOOCOCH}_3 + \text{H}_2\text{O} \]  

(4)

Two schemes (configurations) were proposed in this study for the above process converting ethane to VAM and acetic acid [5, 6]. The evaluation of each scheme was performed on the platform of HYSYS simulation package.

2.1 First Scheme

As shown in Fig. 1, a fresh feed of ethane, which might contain a percentage of methane or higher alkanes, and another fresh feed of oxygen of minimum purity of 99.9% are mixed together with recycle streams, preheated and sent to the first partial oxidation reactor (R-1). This reactor contains a metal oxide catalyst and is operating at a temperature range of 250-300 °C and a pressure in the range of 10-16 bar [5], and where the first three aforementioned reactions take place. The effluent stream from the reactor is cooled down and directed to gas/liquid separator (E-5). This liquid stream, which is mainly consisting of water and acetic acid, is directed to a distillation column (E-6), with 24 theoretical stages, in order to separate acetic acid from water using suitable entrainer [8]. Part of the water can be recycled back to the first reactor in order to increase the selectivity to acetic acid [9, 10]. Acetic acid, taken as a bottom product from column (E-6), is vaporized and mixed with the gaseous stream from unit (E-5). Combined stream enters the second reactor (R-2), at the conditions of 150 to 170 °C and pressure of 4 to 10 bar [11, 12] to undergo the VAM production reaction. The product stream from reactor (R-2) is cooled down and sent to a gas/liquid separation unit (E-11). The liquid stream from unit (E-11) is sent to distillation column (E-13), with 16 theoretical stages, for the recovery of VAM from acetic acid and water while the gaseous stream is directed to CO2 removal unit (E-12). Treated gases from unit (E-12) are recycled back to the first reactor (R-1) after being partially purged to avoid the build-up of non-reacting species in the reactor. Acetic acid from column (E-13) is partially recycled to reactor (R-2). VAM from column (E-13) is further purified to meet required product specifications.
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Fig. 1  Schematic representation for the first configuration of the co-production of VAM and acetic acid: E-1: compressor, E-2: heat exchanger, R-1, R-2: multi-tubular fixed bed reactors, E-4, E-10: coolers, E-5, E-11: gas/liquid separators, E-6: rectification of Acetic acid-Water mixture, E-12: CO₂ removal unit, E-13: distillation column for VAM recovery.

Fig. 2  Schematic representation for the second configuration of the co-production of VAM and acetic acid: E-1: compressor, E-2: heat exchanger, R-1, R-2: multi-tubular fixed bed reactors, E-6: cooler, E-7: gas/liquid separator, E-8: CO₂ removal unit, E-9: distillation column for VAM recovery.
2.2 Second Scheme

The second proposed configuration for the process is shown in Fig. 2. The main difference is that the effluent stream from the partial oxidation reactor (R-1) is sent directly to the second reactor (R-2). The effluent from reactor (R-2) is then cooled down and enters the gas/liquid separator (E-7). The gaseous stream from separator (E-7) is treated and recycled in the same way discussed formerly. VAM is recovered from the liquid stream using distillation column (E-9). The intermediate distillation train of the first configuration is omitted in this case.

3. Process Simulation

Calculations are based on the industrially practiced conversions for various chemical reactions given above. Ethane and oxygen enter the process as fresh feeds with the ratio of 1:1 (ethane to oxygen). Increasing the amount of ethane over that of oxygen in the feed has a negative effect on the overall yield. Oxygen is the limiting reactant and is depleting, resulting in a lower yield of acetic acid and ethylene and hence this will decrease the amount of VAM produced. Explosion limits for various feed and outlet streams from the reactors was also respected and in general a value exceeding 8% oxygen was avoided [12]. To achieve this, the required amount of oxygen was divided between the two reactors and stream of excess oxygen is introduced before the second reactor.

Temperatures and pressures of main process streams follow the industrial values. The temperature approach used in heat exchangers is in the range of 20 to 30 ºC. The fluid package used for most of the process flow sheet is Lee–Kesler Plocker equation of state.

Gas/liquid separation was done on two steps: high pressure and low pressure separation to decrease the amount of escaped gases in liquid streams. Acetic acid is separated from water by using suitable entrainer. Diethyl ether and ethyl acetate were tested and compared. It was found that large amounts of diethyl ether is needed with a column of large number of stages for separation but it has the advantage of being easily recovered from water using a column with a relatively low number of stages. On the other hand, ethyl acetate was more efficient in the separation process of acetic acid, as the purity of product reaches 99% with lower amount of entrainer in a column of 24 theoretical stages. So, ethyl acetate was the selected entrainer for the separation process. It is worth to note that n-butyl acetate and i-butyl acetate are proved to be effective in separating acetic acid-water mixture but using different arrangement other than that used here [13, 14].

Ethylene to acetic acid ratio, in the feed stream of the second reactor, is adjusted to be in the range of 2:1 to 3:1 [11, 12] in order to achieve the required conversion. Gases from gas-liquid separation unit were directed to an absorption column with a stream of acetic acid in order to recover the escaped VAM present in the gaseous stream. In the second scheme, preheating of the feed stream to the first reactor was done on two stages using heater followed by heat exchanger. This technique helps in adjusting the temperature of the effluent stream from the first reactor to enter directly to the second one.

As the reactions are highly exothermic, dilution of the reaction mixture with inert gas is required. This inert gas can be nitrogen or carbon dioxide and the later is more efficient due to its lower heat capacity and positive effect on reaction kinetics [12, 15].

4. Results and Discussion

Simulation was carried for the two proposed configurations. Consolidated values for various process parameters are given in Table 1.

4.1 Effect of Changing the Recycle Ratio on the Overall Yield

The effluent gases from the second reactor can be totally recycled to the first reactor or divided between the two reactors. The recycle ratio is defined as the amount recycled to the second reactor divided by the
Table 1  Typical values of conversions and overall yield resulted from the novel process simulation.

<table>
<thead>
<tr>
<th>Schemes</th>
<th>First reactor</th>
<th>Second reactor</th>
<th>Overall yield&lt;sup&gt;d&lt;/sup&gt; (%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Conversion&lt;sup&gt;a&lt;/sup&gt; (%)</td>
<td>Acetic acid yield&lt;sup&gt;b&lt;/sup&gt; (%)</td>
<td>Ethylene yield&lt;sup&gt;c&lt;/sup&gt; (%)</td>
</tr>
<tr>
<td>Scheme 1</td>
<td>89.76</td>
<td>3.73</td>
<td>2.365</td>
</tr>
<tr>
<td>Scheme 2</td>
<td>85.04</td>
<td>2.91</td>
<td>1.48</td>
</tr>
</tbody>
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<sup>a</sup> Based on oxygen.  <sup>b</sup> Based on ethane.  <sup>c</sup> Based on ethylene.  <sup>d</sup> Overall yield of VAM and acetic acid (based on ethane).

Fig. 3  Amount of VAM/Acetic acid produced versus recycle ratio between the two reactors (fraction recycled to the second reactor / fraction recycled to the first reactor) for the two schemes of the novel process.

amount recycled to the first reactor. Simulation results show that the overall yield was not affected by changing the recycle ratio between the two reactors. Changing this ratio on the other side was found to be useful in control on the ratio of VAM and acetic acid production. As shown in Fig. 3, VAM/Acetic acid ratio increases with increasing the recycle ratio in both schemes. For the same recycle ratio, the first scheme showed a higher ratio of VAM to acetic acid compared to the second scheme.

It is worth to note that the percentage of recycled gases to the first reactor shouldn’t be lower than 73% (with a recycle ratio of 0.358) in order to attain the required reaction conversion in the second reactor.

4.2 Comparison between Two Process Schemes

Simulation results show that changing process variables has directionally the same effect on both schemes. The main advantage of the first scheme is that an optimum amount of water from column (E-6) can be recycled back to the first reactor in order to increase the selectivity to acetic acid. Though, this will increase the separation load on the distillation column. On the other hand, the second scheme has more than one advantage. As shown in Fig. 2, the effluent stream from the first reactor is sent directly to the second reactor thus removing the intermediate separation train. Product purification is thus carried out in one single step saving both in capital and operating costs.

The elimination of this step is a real advantage as azeotropic distillation of acetic acid-water mixture is not an easy separation process. In the second scheme the final distillation column in the separation train will separate the mixture of VAM, acetic acid and water which is considered as a self-entraining system.

Moreover, the pressure of the first reactor is nearly in the same range of the second reactor so; there is no need to have an intermediate compressor in the second scheme. On the other hand, intermediate distillation is carried at atmospheric pressure so re-compression is needed in the first scheme. A numerical relative comparison between the energy loads of both schemes is given in Table 2.

4.3 Advantages of the Novel Process

The new process has many advantages over conventional processes for VAM and acetic acid production:

- Minimum number of equipment is used without having a cracking unit thus highly suitable for small production units.
- Utilities, storage areas and other facilities are combined in one plant instead of having two separate plants for acetic acid and VAM.
Table 2  Energy production and consumption for the two schemes of the novel process.

<table>
<thead>
<tr>
<th></th>
<th>Scheme 1</th>
<th>Scheme 2</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Energy consumption (kW/kmole(^a))</td>
<td>Energy production (kW/kmole(^a))</td>
</tr>
<tr>
<td>Reactors</td>
<td>—</td>
<td>3.95E+5</td>
</tr>
<tr>
<td>Distillation columns</td>
<td>2.925E+6</td>
<td>2.82E+6</td>
</tr>
<tr>
<td>Coolers</td>
<td>9.36E+3</td>
<td>9.75E+3</td>
</tr>
<tr>
<td>Heaters</td>
<td>1.21E+2</td>
<td>1.67E+1</td>
</tr>
<tr>
<td>Pumps</td>
<td>1.65E+5</td>
<td>1.69E+5</td>
</tr>
<tr>
<td>Total</td>
<td>3.1E+6</td>
<td>3.59E+6</td>
</tr>
</tbody>
</table>

\(^a\) On fresh feed basis of 1 kmole of ethane.

- Possibilities of heat integration especially in the second scheme as the products from the first reactor are sent directly to the second one without the need of preheating. Further, the acetic acid vaporizer is eliminated because it is produced in the vapor phase in the first part of the process.
- The process didn’t involve the production of carbon monoxide. Carbon monoxide is poisonous to the catalyst used in the second reactor for VAM production. It also causes serious environmental problems.

5. Conclusions

A novel catalytic process for the co-production of VAM and acetic acid via ethane oxidation was proposed in this study with two different schemes. Simulation results show that the second scheme is more favorable due to its lower fixed and operating cost. The first scheme has the ability of increasing the acetic acid selectivity yet there is an extra separation load. The proposed catalytic process has the advantage of flexibility as the ratio of production of VAM to acetic acid can be easily changed by altering the fraction of gases recycled between the first and the second reactor. Comparing the new process with other conventional processes for VAM or acetic acid production this process shows that the required investment is much lower. As the acetic acid and VAM produced in the same plant, utilities integration and reduced number of equipment will decrease the fixed and operating costs. The process also has the advantage of being environmentally friendly as it doesn’t involve the production of carbon monoxide.

References

Vinyl Acetate from Ethylene, Acetic Acid and Oxygen Industrial Plant Simulation, P. 134650.


