ICCCP 2012: 5-6 May 2012, Kuala Lumpur, Malaysia

Economics of Acetic Acid Production by Partial Oxidation of Ethane

Moustafa Soliman a*, Yousef Al-Zeghayer a,b, Abdulrhman S. Al-Awadi a, Sulaiman Al-Mayman c

a Department of Chemical Engineering, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia
b Director of Industrial Catalysts Chair
Energy Research Institute, KACST, Riyadh, Saudi Arabia

Abstract

Catalysts based on Mo, V, Nb mixed oxides can effect the partial oxidation of ethane to acetic acid. The process requires a pressure of about 20 atm and acetic acid selectivity is about 20%, while ethylene selectivity is about 70%. The addition of Pd to the MoVNb catalyst greatly increases the selectivity to acetic acid to about 80% and completely oxidizes CO to CO₂. In this paper, the economics of acetic acid production by partial oxidation of ethane will be evaluated and compared with the carbonylation of methanol. In particular we study operating fixed bed reactors in series and in two steps. In the first step ethylene is produced and co-produced water is separated. In the second step ethylene is oxidized to acetic acid. This mode of operation increases the concentration of acetic acid leading to great saving in the product cost.

© 2012 Published by Elsevier B.V. Selection and/or peer review under responsibility of Asia-Pacific Chemical, Biological & Environmental Engineering Society
Open access under CC BY-NC-ND license.

Keywords: acid: Economics, Ethane, Ethylene, Acetic Acid, Partial oxidation

1. Introduction

Commercially, acetic acid is mainly produced from methanol carbonylation which gives rise to many problems, such as corrosion and waste disposal. Methanol carbonylation accounts for 65% of the world capacity. Other processes for acetic acid production include oxidation of acetaldehyde, oxidation of naphtha

* Corresponding author
E-mail address: mostf34@hotmail.com
and n-butane and fermentation of hydrocarbons. It is also produced as by-product in the manufacture of cellulose acetate and polyvinyl alcohol. Showa Denko of Japan patented a one-step direct oxidation of ethylene into acetic acid using a palladium-based heteropoly acids catalyst. A 100 KT/year plant based on this patent is working now. In Saudi Arabia, ARAMCO sells methane and ethane to local manufacturers at the low price of $0.75/million Btu. This makes the idea of direct oxidation of ethane to acetic acid very attractive. In 2005, SABIC of Saudi Arabia commercialized a 30,000 tonnes/year acetic acid plant based on a proprietary catalytic oxidation process. The catalyst is a calcined mixture of oxides of Mo, V, Nb and Pd, allowing selectivities to acetic acid as high as 80%. Combining this technology with low cost ethane may result in production economics competitive with methanol carbonylation technology. The main exothermic reaction equations describing the oxidation of ethane are

\[
\begin{align*}
C_2H_6 + \frac{1}{2} O_2 & \rightarrow C_2H_4 + H_2O & \Delta H_{600K} = -24.59 \text{ kcal/mole} C_2H_4 \\
C_2H_6 + \frac{3}{2} O_2 & \rightarrow CH_3COOH + H_2O & \Delta H_{600K} = -116.54 \text{ kcal/mole} CH_3COOH \\
C_2H_6 + \frac{5}{2} O_2 & \rightarrow 2CO + 3H_2O & \Delta H_{600K} = -90.13 \text{ kcal/mole} CO \\
C_2H_6 + \frac{7}{2} O_2 & \rightarrow 2CO_2 + 3H_2O & \Delta H_{600K} = -157.92 \text{ Kcal/mole} CO_2
\end{align*}
\]

The study of MoVNb catalyst for the partial oxidation of ethane to ethylene and acetic acid was pioneered by the work of Thorsteinson et al. [1] and Young and Thorsteinson [2]. The use of high pressure improves the selectivity to acetic acid. The process requires a pressure of about 20 atm and acetic acid selectivity is about 20%, while ethylene selectivity is about 70%. Three patents by Karim et al.[3-5] have been granted to SABIC as a result of work carried out at King Saud University. In these patents, it is shown that the addition of Pd to the MoVNb catalyst greatly increases the selectivity to acetic acid to about 80% and completely oxidizes CO to CO2. The same idea was also discovered by Borchert and Dingerdissen [6]. The mechanism and the kinetics of the reaction for MoV0.25Nb0.12Pd0.0005Ox catalyst were presented by Linke et al. [7,8]. Kinetic expressions for MoVNb catalyst with different compositions are given by Thorsteinson et al [1] and Rahman et al. [9]. Smejkal et al. [10] have analyzed the process of acetic acid manufacture using the MoVNb Pd catalyst and made a comparison between acetic acid production cost by ethane oxidation and methanol carbonylation giving 14% more production cost for the ethane oxidation scheme. With the possibility of continuous catalyst, and reactor design improvements and process design optimization, this difference may be eliminated. On the catalyst improvement side, Ellis [11] found that gold and another elements such as Sn, Ag, Cu, Fe or Sb can replace Pd to increase the selectivity to acetic acid. Brazdil et al. [12] showed that the addition of Sn and Ti to the standard MoVNb catalyst could be used to control ethylene to acetic acid ratio with Ti favoring acetic acid formation. Bergh et al [13] found that Ni, Sb, and Ce could replace Nb. Ryan [14] replaced Nb with Ta & Te. He found that the catalyst has high ethane conversion and ethylene selectivity with very low selectivity to carbon oxides. For oxydehydrogenation reactors design, the main concern is to minimize oxygen concentration in contact with the hydrocarbon to avoid undesired combustion reactions. Several ideas have been explored including Staged Feed of Oxygen (multiple injection points) (Al-Sherehy et al [15]), Membrane Reactors (Tonkovich et al. [16]), Fluidized Bed Reactors (Zeyss et al.[17],cook et al.[18]), Fluidized Bed Membrane Reactors (FLBMR)(Ahchieva et al. [19]), Electrochemical Reactors (Takehra et al.[20]), Cycling Technology based on the redox nature of the catalyst (alternate feed of reactants)(Cavani et al.[21]) and Microchannel Reactors (Brophy et al. [22]). For process design optimization, Rodriguez et al [23] presented a systematic identification procedure. In this paper, we take on the partial oxidation process, and study the economics of certain reactors arrangement.

2. The Partial Oxidation Process Description

A modified Union Carbide process [24] is shown in Fig. 1. Ethane and oxygen are mixed and fed to four
fixed bed reactors in series or a fluidized bed at a temperature of about 550 °K and pressure of 20 atm. The reactors contain a catalyst of mixed oxides of Mo, V, Nb and Pd supported on alumina. Oxygen mole fraction in the feed should not exceed 0.06 to avoid the formation of a flammable mixture. This leads to a low ethane conversion, and this in turn necessitates the use of more than one reactor in series in which fresh oxygen are fed in each reactor. Water vapour favours the formation of acetic acid. Also high pressure and low temperature favour acetic acid formation. The reaction heat is absorbed by pressurized water to generate medium pressure saturated steam. The gaseous product from the last reactor is cooled down to condense part of the acetic acid and water. The remaining acetic acid is removed in a flash chamber or a scrubber using water. The condensed acetic acid and water is sent to an acetic acid concentration plant consisting of a binary distillation column or an azeotropic distillation column which could use ethyl acetate as an entrainer to form an azeotrope with water. The uncondensed product consisting mainly of ethane and CO₂ is recycled. In the original Union carbide process, carbon dioxide is separated using, for example, an amine absorbing and stripping system. Subsequent research indicated that recycling carbon dioxide is economically beneficial.

Fig. 1. Partial oxidation of ethane by total recycle (Four reactors).

The standard oil process (Wagner et al. [25]) is based on a catalyst patented by British Petroleum (Kiston [26]). The catalyst contains a mixed oxide of Mo, V, Nb, Re, Ca, Sb. It has the advantage that in presence of steam vapour, acetic acid selectivity up to 78% can be obtained. Since ethylene CO, CO₂ mole fractions in the reactor effluent are relatively low, one can envisage a process in which the product gases are recycled to the reactor after purging a small portion of that gas. If the reaction is carried out in a fluidized bed reactor, one can feed the oxygen directly into the reactor where it is directly mixed and reacts with ethane. In this way one can use a higher O₂% than that can be used in a fixed bed reactor. This leads to higher ethane conversion. Other advantages that can be gained from this process are as follows:

(i) The elimination of the CO₂ separation system.
(ii) The elimination of the cryogenic separation section to separate ethylene.
(iii) The recycled carbon oxides serve as diluents to absorb the heat of reaction and avoid the formation of flammable mixture.
(iv) The back mixing characteristics of fluidized bed helps increase the selectivity of acetic acid and decrease the selectivity of ethylene.
(v) The heat transfer coefficient in fluidized bed between the reactants and the coolant is much higher in fluidized bed that in fixed bed reactors.

The main disadvantage of this process is that due to the back mixing characteristics of the fluidized bed, we need a bigger reactor volume and thus more of the expensive catalyst than would be required in a fixed bed. Also, because of the need to use water vapor in the reaction system to increase acetic acid selectivity, the acetic acid concentration will be low requiring more expensive acetic acid concentration units.

The following modifications are recently suggested; McSwain and Seaman [27] suggested to treat the effluent of ethane oxidation reactor in a predehydration tower so as to separately recover water, acetic acid, and a gas stream for recycle back to the ethane oxidation reactor. The predehydration tower has 25-35 stages. Johnston et al [28] suggested an integrated, optimized process for the production of ethylene, carbon monoxide and acetic acid from an ethane feed, including reacting ethane with oxygen in the presence of a certain catalyst to produce ethylene, carbon monoxide and acetic acid in a reactor. Carbon monoxide can be made use of in any other chemical reaction, e.g., producing acetic acid through carbonylation of methanol. Ferguson et al. [29] found that if CO is introduced in the feed to the reactor, the amount of CO formed is suppressed. The suppression of CO is not compensated by an equivalent increase in the CO₂ formation, resulting in a net decrease in total carbon oxides (COₓ) formation and an increase in acetic acid selectivity. Ryan and Foster [30] suggested operating two reactors in series one at high temperature (about 450 °C) and the other at low temperature (about 200 °C) to transform any ethylene from the first reactor to acetic acid.

3. Process Economics

Fakeeha et al. [31] studied the process economics of the process with the following modifications on the basic flow sheet, use of air instead of oxygen, changing the inlet temperature of the reactants to the reactor, increasing the number of fixed bed reactors to increase conversion and reduce recycle, and using a fluidized bed reactor. They concluded that oxygen is preferred to air as oxidant. There is an optimum number of reactors resulting from the trade-off between increased conversion and increased capital cost. The study indicated that the number of fixed bed reactors in series with inter-oxygen injection should be four or more. Smejkal et al. [10] concluded also that oxygen should be used as oxidant. They investigated the addition of water vapor to the feed reactors mix. Although the addition of water vapor increases selectivity to acetic acid, the increased cost of separating acetic acid from water indicates that water vapor addition is not recommended. Recycling of the unreacted reactants with CO₂ is recommended. In fact in another paper Rodriguez et al. [23] have shown that the use of a series of reactors with internal recycling reduces the cost of acetic acid production. The use of a fluidized bed followed by a fixed bed reactor is an option that can be studied. The fluidized bed is designed such that not all oxygen is consumed thus reducing catalyst volume. The oxygen remaining is further reacted in the fixed bed. The process economics is studied for the case of acetic acid production. Acetic Acid will be produced at the rate of about 136 Kt/year. In evaluating the economics of the basic flow sheet and its modification the following assumptions are made: Ethane and oxygen supplied are 20 atm., Catalyst life is five years, the location factor for Saudi Arabia is 1.25, and stream factor is 0.9.

| Raw Material Costs: Ethane; 335$/t (equivalent to 0.75 $ / MM Btu), Oxygen: 55$/t, Catalyst: 110 $/kg |
| Utility Costs: Natural gas; 0.75 $/MM Btu, Electricity; 3 c/Kwh, Cooling water (sea water); 30 c/m³, Process water; 125 $/m³. |

The following assumptions are also made: Ethane and oxygen are supplied at 20 atm., Catalyst life is five years, The location factor for Saudi Arabia is 1.25, and stream factor is 0.9.
3.1. Equipment Design

For reactor design, the kinetics for the partial oxidation of ethane is based on the work of Thorsteinson et al. [1] for MoVNb catalyst. The kinetics of acetic acid formation is multiplied by a factor to account for the increased acetic acid selectivity due to the addition of Pd. Reactor simulation was carried out using the model presented by Fakeeha et al [32]. For reactors with ethane flow rate = 0.3 Kg mole/hr tube, O₂ : C₂H₂ = 6 : 94 and coolant temperature = inlet temperature = 550 ºK, the following design parameters are obtained:

- Reactor tube length = 3.0 m
- Reactor tube diameter = 0.0254 m
- Number of tubes in a reactor = 12370 tubes
- Reactor shell diameter = 4.8 m
- Catalyst weight = 103 ton
- Ethane per pass conversion = 10.4%
- Acetic acid selectivity = 74.5%

For the scrubber:

- Cooling and condensing the gas mixture to 44 ºC, Scrubber Inlet Temperature = 44 ºC
- Scrubber Number of Stages = 4
- Acetic acid concentration to the concentration plant = 52% by weight

For acetic acid concentration, Brown [33] reached the conclusion that extraction to be the most favorable approach except for feeds above 80% acetic acid, in which case azeotropic distillation becomes preferable. From this study and that of Brown [33], we established the following formulae for the calculation of the acetic acid concentration section purchased cost (for 2011) and utilities:

\[
\text{Acetic Acid Concentration Plant Purchased Cost} = 70 \times 10^6 / X^{0.7} \text{ $}, \quad X = \text{Weight percent of acetic acid}
\]

\[
\text{Utilities: Electricity} = 50/X \quad \text{Kwt.h/1000 kg Acetic Acid}
\]

\[
\text{Steam} = 60/X \quad \text{Kg/Kg Acetic Acid}
\]

\[
\text{Cooling Water} = 2400/X \quad \text{Kg Water/Kg Acetic Acid}
\]

3.2. Cost Analysis:

Cost estimation using cost data from Peters et al. [34] updated using 2011 chemical engineering plant cost index is given in table 1. In the first column we give cost analysis for the case of using one fluidized. Due to backmixing, the catalyst weight is three times larger than the cases of 4 fixed bed reactors. This accounts for higher product cost. In the second column we give cost analysis for the flow diagram shown in Figure 1 using as catalyst MoVNbPd.

<table>
<thead>
<tr>
<th>Number of Reactors</th>
<th>1 Fluid. Bed</th>
<th>4 Fixed Bed</th>
<th>4 Fixed Bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Inlet Temperature (K)</td>
<td>550</td>
<td>540</td>
<td>700</td>
</tr>
<tr>
<td>Reactor Pressure</td>
<td>40</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>(Ethylene + CO + CO₂) : Ethane Rates</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>Total Capital Investment (MM $)</td>
<td>92</td>
<td>81</td>
<td>74</td>
</tr>
<tr>
<td>Total Product Cost c/kg.</td>
<td>36.0</td>
<td>31.7</td>
<td>29.7</td>
</tr>
</tbody>
</table>

In the third column of table 1, we give cost analysis after carrying out the following modifications:

1- The first two reactors are loaded with MoVNb catalyst and their reactants inlet temperature is above 650 K. At such a temperature the products are ethylene, carbon oxides and water with no acetic acid. The gases are cooled to condense water.

2- The next two reactors are loaded with MoVNbPd catalyst. The gases from the first two reactors after water removal are introduced at about 450-500 K. At this low temperature, ethylene is oxidized to acetic acid with no water production. Water is however produced from the oxidation of ethylene to
carbon oxides. Ethane is not oxidized. The acetic acid concentration could be then as high as 85%. This saves cost of further concentrating the acid.

In table (2), we present the total capital cost calculations for the case of four fixed bed reactors. In table (3), we present total product cost calculations. We notice from table (3) that oxygen contributes strongly to the total product cost. This shows the importance of developing methods for cheaper oxygen production.

Table 2. Purchased equipment cost (MM $).

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Purchased Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactors</td>
<td>2.4</td>
</tr>
<tr>
<td>Heat exchangers</td>
<td>2.8</td>
</tr>
<tr>
<td>Scrubber</td>
<td>0.4</td>
</tr>
<tr>
<td>Recycle compressor</td>
<td>1.5</td>
</tr>
<tr>
<td>Acetic acid concentration</td>
<td>4.4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>11.5</strong></td>
</tr>
</tbody>
</table>

Fixed Capital Investment = Purchased Equipment Cost* Location factor (1.25)* Lang's Factor (4.8) = 69 MM$

Total Capital Investment = Fixed Capital Investment/0.85 = 81 MM$

Table 3. Production cost for acetic acid by ethane partial oxidation (136 Kt/year of acetic acid).

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Quantity / kg.</th>
<th>Price per Unit (c/kg)</th>
<th>Unit Cost (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>0.67</td>
<td>3.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.62</td>
<td>5.5</td>
<td>8.9</td>
</tr>
<tr>
<td>Catalyst</td>
<td>$76 \times 10^{-3}$</td>
<td>11000</td>
<td>1.7</td>
</tr>
<tr>
<td><strong>Total Raw Materials</strong></td>
<td></td>
<td></td>
<td><strong>12.8</strong></td>
</tr>
<tr>
<td>Power</td>
<td>0.1 Kwh</td>
<td>3</td>
<td>0.3</td>
</tr>
<tr>
<td>Cooling Water</td>
<td>0.01 m3</td>
<td>30</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Total Variable Cost</strong></td>
<td></td>
<td></td>
<td><strong>0.6</strong></td>
</tr>
<tr>
<td><strong>Total Direct Fixed Cost</strong></td>
<td></td>
<td></td>
<td><strong>13.4</strong></td>
</tr>
<tr>
<td>(Labor, Maintenance, Plant Overhead, General Expenses,…</td>
<td></td>
<td></td>
<td>13.2</td>
</tr>
<tr>
<td>Depreciation</td>
<td></td>
<td></td>
<td>5.1</td>
</tr>
<tr>
<td><strong>Total Product Cost</strong></td>
<td></td>
<td></td>
<td><strong>31.7</strong></td>
</tr>
</tbody>
</table>

4. Discussion

The production of acetic acid by partial oxidation of ethane is a mature technology the economics of which can be greatly improved, e.g., by further catalyst development, optimization of the operating conditions, better reactor design and energy integration. We notice that the production of one mole acetic acid and one mole of ethylene are associated with the production of one mole of water. Thus, we get more concentrated
acid if we do not produce ethylene. This leads to savings in the acetic acid concentration section. Although water vapor addition to the reactants improves acetic acid selectivity, its expensive separation from product acetic acid makes this undesirable. In fact every effort should be made to reduce the amount of water. The present paper presents a method for reducing the amount of water associated with the acetic acid by oxidizing ethane to ethylene first, then separating water produced followed by oxidation of ethylene to acetic acid.

Co-production of ethylene and acetic acid could be recommended if we could avoid the expensive separation of ethylene from ethane. This can happen if the whole product is further processed to produce vinyl acetate or ethyl acetate without the separation of ethane. The use of a fluidized bed followed by a fixed bed reactor is an option that can be studied. The fluidized bed is designed such that not all oxygen is consumed thus reducing catalyst volume. The oxygen remaining is further reacted in the fixed bed. Smejkal et al. [10] obtained a product cost for acetic acid by carbonylation of methanol of 29c/kg. This can be increased to 34c/kg due to the increase in equipment cost. Thus the partial oxidation process is very competitive with methanol carbonylation. Our estimate and their estimate are very sensitive to the cost of raw materials. They used the following prices 166$/t for methanol, and 50$/t for CO. In our case doubling the price of ethane increases product cost by 2.2c/kg

5. Conclusions

From the study presented in this paper, we conclude that
1. The partial oxidation process is very competitive with methanol carbonylation.
2. Measures should be taken to reduce the amount of water associated with product acetic acid.
3. Cheaper methods for oxygen production need to be developed.
4. Catalyst research is important to improve catalyst performance and lifetime.
5. There is large scope for product cost reduction by process design optimization.

Acknowledgements

The authors acknowledge the support provided by King AbdulAziz City for Science and Technology for the support of this research under grant number AR-29-256.

References


