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Research Article

Improving Purity of Maleic Anhydride Production by Multi-stage Distillation

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Abstract

The maleic anhydride production via benzene oxidation is a highly exothermic reaction which causes the product temperature will increase then it needs to be cooled down with a heat exchanger. The modification process is needed to improve the purity of the maleic anhydride process by adding stage of distillation. Maleic anhydride with lower purity from the first distillation is then distilled again in order to improve its purity. The process modification was simulated using Aspen HYSYS and the comparison of maleic anhydride purity between the basic and the modified process is shown in the form of table based on the material stream. The results obtained that the purity of maleic anhydride for both basic and modified process is about 62.64% and 97.72%. This shows that the modified process has higher maleic anhydride purity compared to the basic process as the purity is closer to 100%. Therefore, this modification increases the maleic anhydride purity of the production through benzene oxidation process.

Keywords: Maleic anhydride; Benzene; Oxidation; Process modification; Multistage distillation; Purity

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1. Introduction

Maleic anhydride (MAN) is an organic compound with the chemical formula $C_4H_2O_3$ which has the form of a white solid in the form of crystal or powder. Synonyms of maleic anhydride is 2,5-Furandione, cis-Butenedioic anhydride, Dihydro-2,5-dioxofuran, Maleic acid anhydride, and Toxilic anhydride. Maleic anhydride is hygroscopic, easily absorbs moisture from the air, and reacts with water to form maleic acid. This compound has a melting point of 53 °C and a boiling point of 200 °C [1,2]. Maleic anhydride is also reactive with amino groups, alcohols, compounds that have double bonds, high acidity, low melting point, abundant carboxyl group content, and the presence of unsaturated bonds after the ring opening process. These characteristics make maleic anhydride very suitable for various commercial applications, such as surface coatings, water filtration systems, drug carriers, food packaging, hydrogels for wound care, and biomedical applications [3]. In addition, MAN is also widely used in the production of other chemicals, such as polyester resins, food additives, agrochemicals, and pharmaceutical products. MAN can also be utilized in the synthesis of polyurethanes, as a more environmentally friendly alternative to petroleum-based materials, as well as to improve the thermal and mechanical properties of polyurethanes through copolymerization with monomers such as styrene or acrylonitrile. [4-6].

The maleic anhydride (MAN) production process is based on two different technological processes in the gas phase, namely benzene oxidation and n-butane oxidation. Selective oxidation of benzene results in the loss of two

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carbon atoms, reduces mass yield, and produces heavy by-products such as phthalic anhydrous and benzoquinone. In contrast, in n-butane oxidation, lighter by-products such as acetic acid and formic acid are obtained. The difference in these technologies also lies in the operating conditions which are influenced by several factors such as feedstock conditions and process design. The type of reactor used can be fixed, fluidized, or a moving bed. The recovery of maleic anhydride can be done in both aqueous and organic phases, and the purification can be done through azeotropic distillation or thin-film evaporation [7-10]. In addition, MAN can also be produced by converting biomass platform compounds such as furfural and butanol [11].

The synthesis of MAN involves the selective oxidation of benzene in the gas phase, at a temperature between 350–450 °C. The reaction is catalysed by mixed oxides of vanadium and molybdenum (V_2O_5 and MoO_3) supported by inert materials. It allows obtaining a selectivity of MA equal to 74% with a conversion of benzene estimated at around 96–98%. while the oxidation of n butane uses a C4 alkane catalyst in the presence of vanadyl pyrophosphate as a catalyst ($VO_2P_2O_7$). It consists of mixed oxides of phosphorus and vanadium (IV). Depending on the type of technology used for the synthesis, the selectivity of MA reaches 53–65% and the conversion of n-butane does not exceed 90% [12].

Maleic anhydride (MAN) is a chemical product that has a wide market due to its application as an intermediate to produce unsaturated polyester resins, polymers, varnishes and paints, as well as several other commodities. In 2015, the global capacity of MAN production amounted to 2800 million metric tons [13]. In 2017, the global demand for MAN was estimated at 1.8 million tons and is projected to increase to 2.2 million tons by 2023, with a compound annual growth rate of 3.69%. The global MAN market is dominated by the Asia-Pacific region [14]. Since 1984, MAN market volume has shown a significant increase, with annual global production reaching 2.88 million tons in 2019. Despite a small decline between 2020 and 2021 (approximately 2.76 to 2.79 million tons), most likely due to the impact of the COVID-19 pandemic, it is estimated that total production will increase to 3.40 million tons in 2029 [12].

Improving the purity of maleic anhydride is essential to enhance its performance and application in various industries, including the production of plastics, resins, and pharmaceuticals. One of the main methods to achieve higher purity is through optimization of the manufacturing process, specifically during the oxidation of benzene or butane. Efforts to improve the quality of MAN can also be made by reducing color and improving thermal stability. In previous studies, to increase the purity of MAN, a three-stage distillation process was used. In a simplified version of this solvent process, the waste MAN from the reactor is brought into contact with organic solvents in an absorber. This process reportedly reduces solvent decomposition and can increase the yield of MAN in the 97-99% range [15]. The advantages of a solvent recovery section coupled with a continuous distillation over an aqueous and batch purification section are elimination of the by-product formation of acids, reduced steam consumption, reduced liquid effluent, superior MAN quality [16].

In this case, the proposed innovation is to use a two-stage distillation process to improve the purity of MAN obtained through benzene oxidation using Aspen HYSYS for process simulation and modification. This modification aims to produce MAN with higher purity compared to the unmodified process. By applying two-stage distillation, it is expected to increase the separation efficiency and quality of MAN produced, resulting in more optimal results in production.

2. Methods

2.1 Oxidation

Oxidation is a chemical process where a substance loses electrons, leading to an increase in its oxidation state. This is often accompanied by the gain of oxygen or the loss of hydrogen in a chemical reaction. Oxidation is a fundamental concept in redox (reduction-oxidation) reactions, where one substance is oxidized, and another is reduced [17]. One of the ways to produce maleic anhydride is through benzene oxidation (Figures 1 and 2).

The oxidation of benzene to maleic anhydride is an industrial process where benzene reacts with oxygen in the presence of a vanadium pentoxide (V_2O_5) catalyst at high temperatures (400–500 °C) (Figure 1). The reaction produces maleic anhydride ($C_4H_2O_3$), carbon dioxide (CO_2), and water (H_2O) as byproducts, as shown in the equation:

$$C_6H_6 + 4.5O_2 \rightarrow C_4H_2O_3 + 2CO_2 + H_2O \quad \Delta H^o_{298K} = -1377.9 \text{ kJ/mol} \qquad (1)$$

This highly exothermic process involves passing a mixture of benzene vapor and air over the catalyst, with the maleic anhydride recovered by cooling or absorption [14]. While historically significant, the benzene route has largely been replaced by the more economical and environmentally friendly oxidation of n-butane.

2.2 Method to Improve Purity of Maleic Anhydride

To obtain a high-purity maleic anhydride, bottom product of absorber must be applied into the distillation operation. Multistage distillation is proposed as an addition to the single-stage distillation operation on the basic process. The top product of the distillation (Stream 11) which contains maleic anhydride and water undergoes the second stage of distillation (T-102) to obtain higher purity of maleic anhydride. Aspen HYSYS V11 is used to simulate and modify the production of maleic anhydride through benzene oxidation. The results are then compared and analyzed to conclude the effect of the addition of distillation stage against the purity of maleic anhydride.

3. Results and Discussion

3.1 Comparison Between Basic and Modified Processes

Mass and energy balances of the modified process are reported in Table S1 (Supporting Information). The simulation of maleic anhydride production through benzene oxidation process for basic and modified process using Aspen HYSYS is depicted in Figures 3-6. The basic process simulation is shown in Figure 3, while the PFD of the basic process is shown in Figure 5. In the basic process, less equipment is used only a single stage distillation. Whereas the modified process simulation is shown in Figure 4, while the PFD is shown in Figure 6. In the modified process, more equipment is used due to additional stage of distillation. The difference between those two is in the number of distillation stages which can be seen in the modified process. On the basic process, there is only a single stage distillation, therefore resulting in relatively low purity of maleic anhydride, which contains about 37.36% mol of water, but for the modified process, there is an additional stage of distillation which improves the purity of the obtained maleic anhydride as high as 97.92% mol.

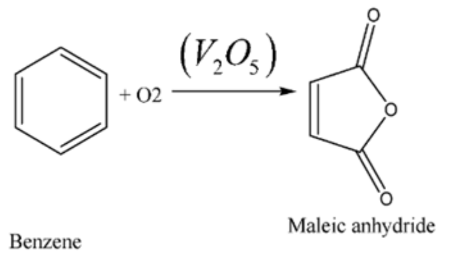

Figure 1. Oxidation of benzene

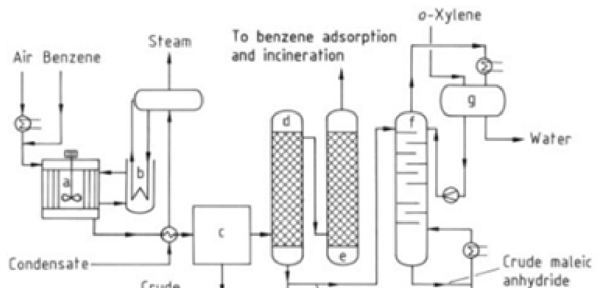

Figure 2. Simplified block diagram of maleic anhydride via benzene oxidation [14].

3.2 Thermodynamics Review

Oxidation benzene to maleic anhydride reaction can be expressed as:

$$C_6H_6 + 4.5O_2 \rightarrow C_4H_2O_3 + 2CO_2 + H_2O \quad \Delta H^o_{298K} = -1377.9 \text{ kJ/mol} \quad (2)$$

For the determination of the nature of the reaction (exothermic / endothermic) and the direction of the reaction (reversible / irreversible), it is necessary to calculate the standard heat of reaction (ΔH^o_{298K}) at 1 bar and 298 K based on standard heat of formation of the reactants and products. The value of $\Delta H_f°$ and $\Delta G_f°$ can be seen in Table 1 [18].

Standard heat of reaction at 298K (ΔH^o_{298K}):
$\Delta H^o_{298K} = \Sigma\Delta H_f°$ product - $\Sigma\Delta H_f°$ reactant
$= (\Delta H_f°\ C_4H_2O_3 + \Delta H_f°\ CO_2 + \Delta H_f°\ H_2O) - (\Delta H_f°\ C_6H_6 + \Delta Hf°\ O_2)$
$= (-398.3 + 2(-393.5) + (-241.8)) – (-49.2 + 0) = -1377.9$ kJ/mol

Based on the calculations, we get the value $\Delta H^o_{298K} = -984.4$ kJ/mol, which is a negative value so that the reaction is exothermic.

Gibbs energy (ΔG^o_{298K}):
$\Delta G^o_{298K} = \Sigma\Delta G_f°$ product - $\Sigma\Delta G_f°$ reactant
$= (\Delta G_f°\ C_4H_2O_3 + \Delta G_f°\ CO_2 + \Delta G_f°\ H_2O) - (\Delta G_f°\ C_6H_6 + \Delta Gf°\ O_2)$
$= (-355 + 2(-394.4) + (-237.14)) – (129.8+ 0)$
$= -1510.74$ kJ/mol

Table 1. The value of $\Delta H_f°$ and $\Delta G_f°$ of compounds

Compounds	Molecular Formula	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)
Benzene	C_6H_6	-49.2	129.8
Oxygen	O_2	0	0
Maleic anhydride	$C_4H_2O_3$	-398.3	-355
Carbon dioxide	CO_2	-393.5	-394
Water	H_2O	-241.8	-237.14

Equilibrium constant (K_2) in the standard state:
$\Delta G^o_{298K} = -RT \ln K$

$$\ln K_2 = -\frac{\Delta G^O_{298K}}{RT} = \frac{-1510740 \frac{\mathrm{J}}{\mathrm{mol}}}{8.314 \frac{\mathrm{J}}{\mathrm{mol}} \cdot 298K} = 609.766$$

$K_2 = 6.579 \times 10^{264}$

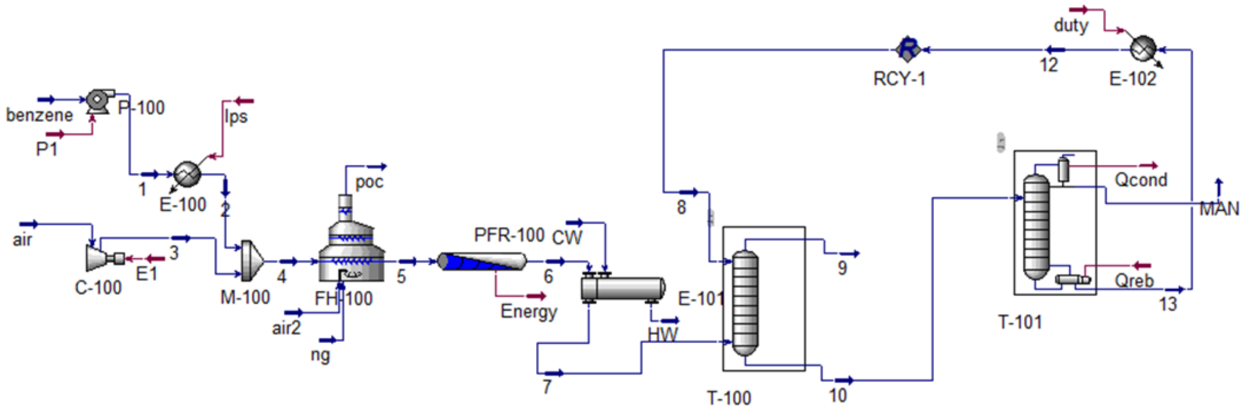

Figure 3. Simulation using Aspen HYSYS of basic (unmodified) process

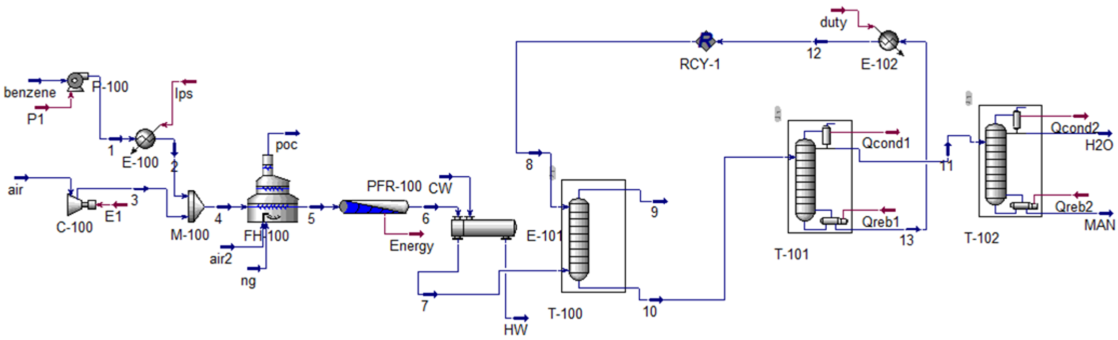

Figure 4. Simulation using Aspen HYSYS of the modified process

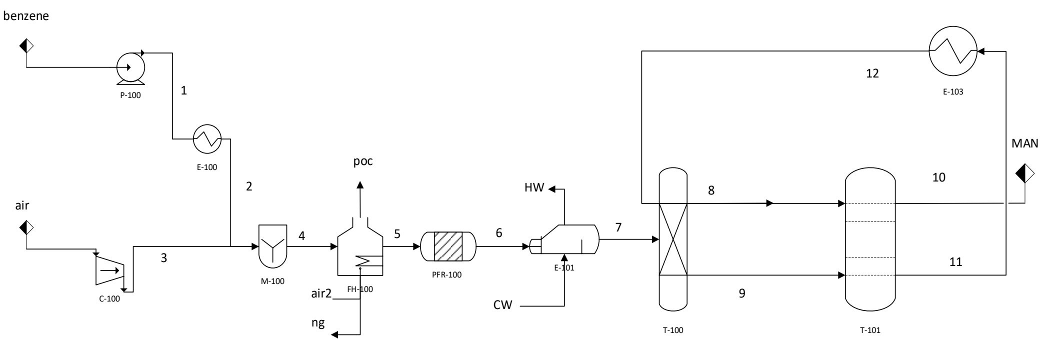

Figure 5. Process flow diagram of the basic (unmodified) process [20]

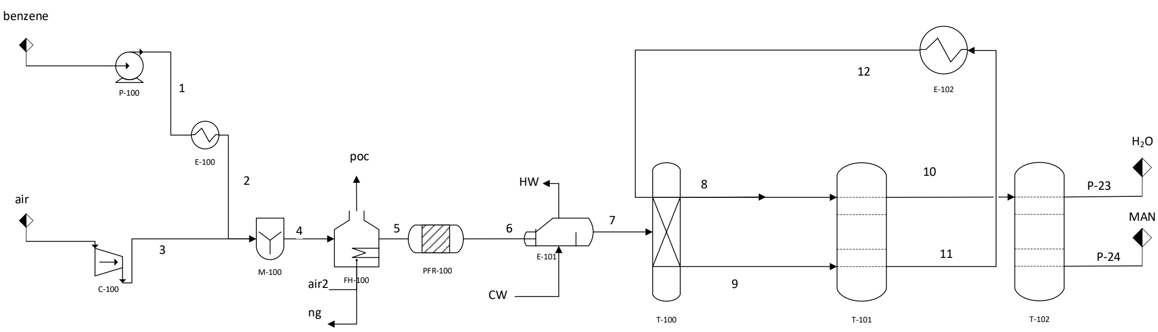

Figure 6. Process flow diagram of the modified process

Equilibrium constant (K_1) at reactor temperature T = 406 °C:

$$\ln\frac{K_1}{K_2} = \frac{-\Delta H_R^O}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

ΔH^o_{298K} = Standard heat of reaction at 25°C

$$\ln\frac{K_1}{6.579 \times 10^{264}} = \frac{1377900\ \frac{\mathrm{J}}{\mathrm{mol}}}{8.314\ \frac{\mathrm{J}}{\mathrm{mol.K}}}\left(\frac{1}{652\,K} - \frac{1}{298\,K}\right)$$

$$\ln\frac{K_1}{6.579 \times 10^{264}} = -301.958$$

$K_1 = 4.779 \times 10^{133}$

Since the value of the equilibrium constant is relatively large, the reaction is irreversible, only the formation of product occurred during reaction.

3.3 Two-Stage Distillation of Maleic Anhydride to Obtain Higher Purity

Maleic anhydride formed after the reaction (PFR-100) is cooled with a heat exchanger from 1335 °C to 39.26 °C using cooling water (CW). The output is then absorbed through an absorption column (T-100) using dibutyl phthalate. Subsequently, the absorbed maleic anhydride is distilled with two-stage distillation columns (T-101 and T-102) which results in high purity maleic anhydride. Table 2 shows the difference of maleic anhydride mole fraction obtained from basic process and modified process.

Based on the comparation showed on the Table 2, it can be concluded that an addition of distillation column into the basic process improves the maleic anhydride obtained. The first distillation column focused on removing the dibutyl phthalate from the absorption process in order to be fed into the absorber column again in the recycle stream, then the added distillation column aims to separate MAN from the remaining water contained.

4. Conclusion

Two-stage distillation improves the purity of obtained maleic anhydride through oxidation of benzene. On the unmodified process, maleic anhydride only has purity of 62.64 %mole, meanwhile the modified process results in higher purity, that is 97.72 %mole.

Table 2. Difference of maleic anhydride mole fraction obtained from basic process and modified process

Process	Mole fraction of maleic anhydride	Mole fraction of water
Basic	0.6264	0.3736
Modified	0.9772	0.0228

References

[1] Hartwig, A., Commission, M.A.K. (2023). Maleic anhydride. *The MAK Collection for Occupational Health and Safety,* 8(1), DOI: 10.34865/mb10831e8_1ad.

[2] Hernández-Moreno, D., de la Casa Resino, I., Soler-Rodríguez, F. (2014). Maleic Anhydride. *Encyclopedia of Toxicology,* 13, 138–141. DOI: 10.1016/b978-0-12-386454-3.01185-4.

[3] Huang, Y., Jin, T., Zeng, H., Liu, L., Xu, K., Chai, X., Zhang, L. (2023). Development of novel sustainable hyperbranched polyester wood adhesives from glycerol and maleic anhydride by solvent free method. *Industrial Crops and Products*, 204, 117326. DOI: 10.1016/j.indcrop.2023.117326.

[4] Ali, E., Ali, M.A.H., Alhumaizi, K., Elharbawi, M. (2017). Optimal oxygen feeding policy to maximize the production of Maleic anhydride in unsteady state fixed bed catalytic reactors. *Journal of King Saud University-Engineering Sciences*, 29(3), 204-211. DOI: 10.1016/j.jksues.2015.12.001.

[5] Savani, N.G., Naveen, T., Dholakiya, B.Z. (2023). A review on the synthesis of maleic anhydride-based polyurethanes from renewable feedstock for different industrial applications. *Journal of Polymer Research*, 30(5), 175. DOI: 10.1007/s10965-023-03543-7.

[6] Agirre, I., Gandarias, I., Granados, M.L., Arias, P.L. (2020). Process design and techno-economic analysis of gas and aqueous phase maleic anhydride production from biomass-derived furfural. *Biomass Conversion and Biorefinery*, 10(4), 1021-1033. DOI: 10.1007/s13399-019-00462-w.

[7] Mangili, P.V., Junqueira, P.G., Santos, L.S., Prata, D.M. (2019). Eco-efficiency and techno-economic analysis for maleic anhydride manufacturing processes. *Clean Technologies and Environmental Policy*, 21, 1073-1090. DOI: 10.1007/s10098-019-01693-1.

[8] Müller, M., Kutscherauer, M., Böcklein, S., Mestl, G., Turek, T. (2020). On the importance of by-products in the kinetics of n-butane oxidation to maleic anhydride. *Chemical Engineering Journal*, 401, 126016. DOI: 10.1016/j.cej.2020.126016.

[9] Papracanin, E., Dozic, A., Mujkic, E., Hodzic, M., Hodzic, I., Poljic, B., Ramic, A. (2022). Separation of fumaric and maleic acid crystals from the industrial wastewater of maleic anhydride production. *Hungarian Journal of Industry and Chemistry*, 50(2), 1-6. DOI: 10.33927/hjic-2022-10.

[10] Wojcieszak, R., Santarelli, F., Paul, S., Dumeignil, F., Cavani, F., Gonçalves, R.V. (2015). Recent developments in maleic acid synthesis from bio-based chemicals. *Sustainable Chemical Processes*, 3, 1-11. DOI: 10.1186/s40508-015-0034-5.

[11] Li, H., Wu, P., Li, X., Pang, J., Zhai, S., Zhang, T., Zheng, M. (2022). Catalytic hydrogenation of maleic anhydride to γ-butyrolactone over a high-performance hierarchical Ni-Zr-MFI catalyst. *Journal of Catalysis*, 410, 69-83. DOI: 10.1016/j.jcat.2022.04.011.

[12] Cucciniello, R., Cespi, D., Riccardi, M., Neri, E., Passarini, F., Pulselli, F.M. (2023). Maleic anhydride from bio-based 1-butanol and furfural: a life cycle assessment at the pilot scale. *Green Chemistry,* 25, 5922–5935. DOI: 10.1039/d2gc03707f.

[13] Mestl, G., Lesser, D., Turek, T. (2016). Optimum Performance of Vanadyl Pyrophosphate Catalysts, *Topics in Catalysis*, 59, 17-18. DOI: 10.1007/s11244-016-0673-0.

[14] Yu, T.Y., Kuo, C.T., Lai, C.K., Won, W., Yu, B.Y. (2024). Unraveling the alternative process configurations for more environmentally friendly Maleic Anhydride production. *Process Safety and Environmental Protection*, 191, 2385-2401. DOI: 10.1016/j.psep.2024.09.116.

[15] Musa, O.M. (2016). *Handbook of Maleic Anhydride Based Materials Syntheses, Properties and Applications.* Switzerland: Springer International Pubblishing. DOI: 10.1007/978-3-319-29454-4_1.

[16] Novelli, M., Leonardi, M., Cortelli, C. (2014). *Selective Oxidation Reactions in Polynt: An Overview of Processes and Catalysts for Maleic Anhydride*. Handbook of Advanced Methods and Processes in Oxidation Catalysis, 334–352. DOI: 10.1142/9781848167513_0014.

[17] Yaws, C.L. (1999). *Chemical Properties Handbook.* NewYork: Mc Graw Hill Handbooks.

[18] Samimi, J. (2023). Evolution of the Oxidation Reaction and its Stability. *Journal of Thermodynamics & Catalysis,* 14(6). DOI: 10.32548/2157-7544.23.14.363.

[19] Ullman, F. (2003). Ullman's Encyclopedia of Industrial Chemistry. DOI: 10.1002/14356007.

[20] Turton, R., Shaeiwitz, J.A., Bhattacharya, D. (2018). *Analysis, Synthesis, and Design of Chemical Processes Fifth Edition*. Michigan: Prentice Hall.