

Article

Performance Comparison of Industrially Produced Formaldehyde Using Two Different Catalysts

Kamran Shakeel ¹, Muqaddam Javaid ¹, Yusra Muazzam ¹, Salman Raza Naqvi ^{1,*} , Syed Ali Ammar Taqvi ^{2,3} , Fahim Uddin ², Muhammad Taqi Mehran ¹, Umair Sikander ¹ and M. Bilal Khan Niazi ¹

¹ School of Chemical & Materials Engineering, National University of Sciences & Technology, Islamabad 44000, Pakistan; kshakeel_che08@scme.nust.edu.pk (K.S.); muqaddam96@gmail.com (M.J.); ymuazzam_che08@scme.nust.edu.pk (Y.M.); taqimehran@scme.nust.edu.pk (M.T.M.); umair.sikandar@scme.nust.edu.pk (U.S.); m.b.k.niazi@scme.nust.edu.pk (M.B.K.N.)

² Department of Chemical Engineering, NED University of Engineering & Technology, Karachi 75270, Pakistan; aliammar@neduet.edu.pk (S.A.A.T.); fahimuddin@neduet.edu.pk (F.U.)

³ Chemical Engineering Department, Universiti Teknologi PETRONAS, Perak 32610, Malaysia

* Correspondence: salman.raza@scme.nust.edu.pk

Received: 25 September 2019; Accepted: 21 October 2019; Published: 12 May 2020



Abstract: Formaldehyde is an important industrial chemical that is a strong-smelling and colorless gas. It is used in a number of processes such as making household products and building materials, glues and adhesives, resins, certain insulation materials, etc. Formaldehyde can be produced industrially using air and methanol as raw materials in the presence of metal oxide catalyst or silver-based catalyst. The operating conditions and requirements of the process depend on the type of catalyst used. Therefore, a comparative study of both processes was conducted, and the results were compared. It was observed that the silver-based catalyst process has a compact plant size since the amount of air required is halved as compared to the metal oxide process. Thus, it appears that the silver-based catalyst process is more suitable for small-scale production due to its compact size and reduced utility cost.

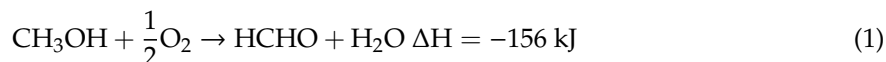
Keywords: Formox Perstorp; formalin; fixed catalytic bed reactor; silver catalyst; metal oxide catalyst

1. Introduction

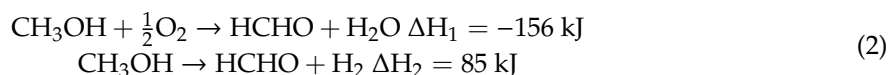
The extensively used formaldehyde is produced by using air and methanol as the raw materials. The reaction occurs in the reactor in the presence of a catalyst. The resulting products of the reaction are formaldehyde and water [1]. Then the mixture of products and unreacted reactants goes to the absorption column where water is showered from the top. The bottom product is formalin i.e., a 37% aqueous solution of formaldehyde [2]. The unreacted reaction mixture is removed from the top [1,3–7]. The extensive range of applications of formaldehyde makes it a valuable chemical. It may be used in different industries such as domestic, medical, cosmetics, and the textile industry [8–10].

The consumption and demand of formaldehyde is increasing. Formaldehyde is the principal component for the production of resins, phenols, urea, and melamine [11]. It is used for weather resistance i.e., in adhesives and wood coatings [12]. In addition, it has a disinfectant property; it is present in soaps as a disinfectant. In medical fields, formaldehyde is used for the sterilization of the surgical instruments. It imparts the resistance to fabric against crumples. In cosmetic products, formaldehyde is used as a preservative since it enhances the effectiveness of products against different microorganisms. It is used in glue production for household use. Formaldehyde is used in the manufacturing of plastics, carpets, and vaccines, etc. In plastic utensils industry, it is the major component [13].

Commercially, formaldehyde is produced mostly from air and methanol as raw materials using three different methods. In the first method, formaldehyde is produced using air and methanol in the presence of molybdenum oxide catalyst present inside the tubes of shell and tube reactor [14]. The reacting mixture enters at tube side to interact with catalyst forming the product [15].



The second method involves the production of formaldehyde in the presence of silver oxide catalyst present in fixed catalytic bed reactor [16].



In third method, formaldehyde is produced using oxidation of methane and other hydrocarbons [17]. The separation processes and reaction mechanism in the above three methods are almost the same. For commercial production of formaldehyde, process optimization is required.

Lefferts et al. studied the production process of formaldehyde through oxidative hydrogenation of methanol in the presence of silver catalyst [18]. They studied the effect of temperature, gas velocity, and concentration of both reactants on the production process. They developed the reaction model based on the experimental data and explained the impact of form and composition of silver catalyst over methanol conversion. Yang et al. used molybdenum oxide catalyst supported over silica for the oxidation of methanol to formaldehyde [19]. Their study was based on the selectivity and activity of N_2O and O_2 used as oxidants. They observed that N_2O is responsible for the oxidation of carbon monoxide. Moreover, the supported molybdenum catalyst has higher activity than the non-supported catalyst. Qian et al. explained the formaldehyde synthesis process using polycrystalline silver catalyst [20]. They compared the water ballast process with the methanol ballast process and observed an increased selectivity of formaldehyde in the absence of water. Moreover, the selectivity of the product is highly temperature dependent. Moreover, Waterhouse et al. used SEM techniques to determine the relationship between morphology of silver catalyst and its performance [21].

In this study, a performance comparison of the industrially produced formaldehyde using two different catalysts is presented. Real-time industrial data are collected from a local industry in Pakistan, and material and energy balances, simulations, and cost analysis are executed. We have compared the two different catalysts based on material and energy balances, the size of the plant, the installation, and utility cost.

2. Materials and Methods

2.1. Material and Energy Balance

The steady-state material balance calculation is done for both processes. It was assumed that there was no accumulation in the system and there was no change with respect to time. The total amount of material in and out is almost the same. The basis for calculations were considered to be one day of operation i.e., 90 tons of formalin is produced in one day.

The energy balance calculations involve calculation of ΔH at both inlet and outlet sides. The reference temperature was 25°C . Since the entering and leaving streams are mixtures of components, average heat capacity ($C_{p,\text{avg}}$) was calculated by the product of mole fraction (x_i) of the component in the mixture and its individual heat capacity (C_p). The change in temperature was calculated by the subtraction of the stream temperature with the reference temperature. The overall enthalpy content was found by taking the difference of the total heat content at the outlet and the inlet. The heat

of the reaction was incorporated in the energy balance of the reactor and heat of condensation of formaldehyde was included in the energy balance around the absorption column.

$$\Delta H = mC_{p_{avg}}\Delta T \quad (3)$$

2.2. Cost and Payback Period

The equipment and utility costs were calculated from Aspen Plus[®]. Then, the different incorporating factors like piping, instrumentation, buildings, and total physical plant cost were calculated. Then, total fixed capital was determined by incorporating some other factors like design and engineering, contractor's fee, and contingency. After that, working cost was calculated, which is 5% of total fixed capital. Then, the total investment was determined by adding working cost and total fixed capital.

$$\text{Total Investement} = \text{Working Capital} + \text{Total Fixed Cost} \quad (4)$$

Revenue was calculated by multiplying the amount of formalin produced by price of formalin.

$$\text{Revenue} = \text{Price of Formalin (kg)} \times \text{Formlain Produced (kg/year)} \quad (5)$$

The cost of raw material and catalyst was determined by multiplying the quantities (units) consumed per year by price per unit.

Then, profit was calculated by subtracting all the expenses from the revenue and payback period was determined.

$$\text{Payback Period} = \frac{\text{Total Investment}}{\text{Profit}} \quad (6)$$

3. ASPEN Flow Sheets

Based on real time industrial data, simulations are performed for the both processes using ASPEN PLUS[®] V8.8. Methanol, oxygen, nitrogen, silver, and molybdenum were selected as the components for simulation. For both the process, non-random two liquids (NRTL) was selected as the fluid package. The mixture of air and methanol is preheated and then sent to the reactor. The reaction mechanism that produces the formaldehyde depends upon the type of catalyst used. The product stream is sent to the adsorption column where it is treated with water to separate the desired product. The simulation models are explained in Sections 3.1 and 3.2.

3.1. Simulation Model of Molybdenum-Based Formaldehyde Process

Figure 1 presents the simulation of Molybdenum-based process on ASPEN PLUS. Non-random two-liquid model (NRTL) is used as the fluid package. The air and methanol are used as starting materials. Methanol and air both are initially mixed and passed to pre-heater where the temperature of the mixture increases from 27 °C to 107 °C. The mixture is passed to the reactor. The reactor is a shell and tube type reactor. The reaction mixture enters the reactor in catalyst-filled tube sides at 107 °C. The reaction occurs here and water and formaldehyde are produced. The shell side contains DTH (Dowtherm heat transfer media), which is used to extract the excess heat of the reaction i.e., the reaction is exothermic producing 159 KJ/mol of the energy. The boiling point of DTH is around 260 °C and same is the temperature inside the reactor, so the DTH leaves the reactor shell side as vapors. DTH goes to the condenser where the DTH vapors condense back to liquid state and accumulated in DTH tank. Upon requirement, DTH again goes to the reactor and the cycle continues. The mixture (product and unreacted reactants) leaving the tube side is at 280 °C. Since this mixture is at a very high temperature, so the heat of this mixture can be utilized. This mixture goes to the shell side of the pre-heater to heat the incoming reaction mixture. After pre-heating the incoming mixture, it leaves the shell side of preheater at 150 °C and goes to the absorption column from bottom side. Water at 37 °C is showered from the top of the absorption column. The amount of water showered is very critical as it

produces the required concentration of the final product. The formalin is removed from the bottom. The temperature of the exiting product is 27 °C. The unreacted reaction mixture i.e., CH_3OH , O_2 , N_2 is removed as off gas from top of absorption column at 23 °C.

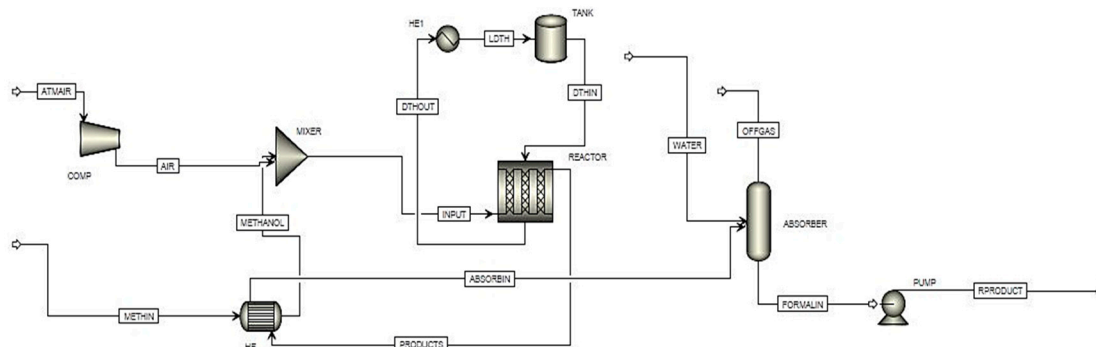


Figure 1. Simulation model of Molybdenum-based formaldehyde process.

3.2. Simulation Model of Silver-Based Formaldehyde Process

Figure 2 presents the ASPEN PLUS simulation of silver-based formaldehyde process. NRTL was selected as the fluid package. The reaction temperature for this process is around 600–650 °C. This process does not incorporate the DTH cycle. The air is passed through a compressor and then mixed with methanol using a mixer. The reacting mixer goes directly into the reactor from the mixer as a pre-heater is not used in this process. The reactor is a fixed bed catalyst type of reactor incorporating the bed of catalyst. The reaction occurs at the catalytic bed and quenching water is used at the bottom of reactor to cool down the product. The mixture of products and unreacted reactants enters the absorption column from bottom where water is showered from top. The unreacted reaction mixture is removed from the top as off gas, air is recycled from this off gas and again passed to the mixer while the product is removed from bottom. The product goes to the distillation column where separation takes place and we get formalin as a bottom product and methanol as a top product, which is then recycled.

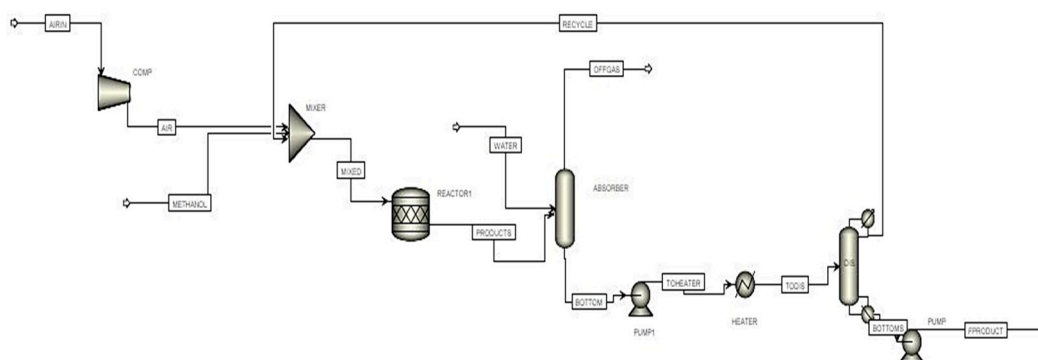


Figure 2. Simulation model of silver-based formaldehyde process.

4. Catalyst Properties

The properties of the molybdenum oxide and silver oxide catalyst used in the production process are shown in Table 1. It can be observed that the conversion of the molybdenum oxide-based plant is 99% and that of the silver oxide-based plant is 85%. The life of the molybdenum oxide catalyst is 12–18 months and that of the silver oxide-based process is 3–8 months. The porosity of the molybdenum oxide catalyst is 0.7 and that of the silver oxide catalyst is 0.5.

Table 1. Properties of catalyst.

Properties	Molybdenum Oxide	Silver Oxide
Methanol Conversion	99%	85%
Utilization time	12–18 months	3–8 months
Regeneration	Difficult	Convenient
Porosity	0.7	0.5

The life of the silver catalyst is highly dependent upon the operating conditions of the formaldehyde reactor. Silver catalysts in the formaldehyde plant are typically used for a period of a few months to a year depending on the reaction temperature and pressure [22]. Generally, sintering occurs in the silver catalyst due to reaction temperatures, which results in high pressure drop over the bed, which decreases the performance of catalyst. It is observed that the water ballast process prolongs the life of catalyst by introducing water with its associated high heat capacity that equally distributes the heat over the catalyst bed resulting in minimizing coke formation and sintering [23,24]. Our objective is the performance comparison of both processes based on the plant size, installation and utility cost, and material and energy balance.

5. Results and Discussion

The results in this section include the materials and energy balance of both plants, costing, payback period, and comparison on the basis of size for the two catalytic processes. Section 5.3 presents the discussions on the results.

5.1. Material and Energy Balance

The materials and energy balance sheets that were obtained from Aspen Plus® are given in Sections 5.1 and 5.2.

5.1.1. Material Balance of Molybdenum Oxide

The material balance of Molybdenum Oxide catalyzed process is shown in Table 2. The table shows the flow rates and densities of all of the components of the process. The methanol in inlet stream is 46.25 kmol/h. The flow rate of oxygen in the inlet air stream is 27.56 kmol/h. The formaldehyde in the product stream is 45.7875 kmol/h.

5.1.2. Energy Balance of Molybdenum Oxide

The energy balance of Molybdenum oxide process is shown in Table 3. The table shows the temperatures, pressures, and enthalpies of all the components of the process. The pressure varies from 1 bar to 1.8 bar during the process and temperature varies from 25 to 246.69 °C during the process. The input air has a temperature of 25 °C and the temperature of DTH going out of condenser is 246.69 °C. The enthalpy in reactor is −18,685.22 cal/mol. The highest pressure during the process is inside the absorption column, which is 1.8 bar.

5.1.3. Material Balance of Silver Oxide

The materials and energy balance of the silver oxide catalyzed process obtained from aspen plus is shown in Table 4. The table shows the material balance for silver oxide plant. The molar flow rate of oxygen in the air stream is 14.28 kmol/h. The molar flow rate of methanol in the inlet stream is 49.5 kmol/h. The formaldehyde in the product stream is 46.728 kmol/h.

Table 2. Material balance of Molybdenum-based process.

Stream ID	A2	AIR	DTHIN	DTHOUT	GH	INPUTAIR	LIQUID	METHANOL	METHIN	OFFGAS	PRODOUT	REACIN	TOTANK	WATER
From	ABSORBER	MIXER	HEATEX1	CONDENSR	EX2	COMP		MIXER	EX2		HEATEX1	REACTOR1	TANK	ABSORBER
To	EX2	COMP	TANK	HEATEX1	HEATEX1		ABSORBER	EX2		ABSORBER	REACTOR1	MIXER	CONDENSR	
Phase	MIXED	VAPOR	LIQUID	LIQUID	VAPOR	VAPOR	LIQUID	MIXED	LIQUID	VAPOR	VAPOR	VAPOR	LIQUID	LIQUID
METHA-01 (kmol/h)	0.4625	0	0	0	0.4625	0	0.4625	46.25	46.25	3.71×10^{-234}	0.4625	46.25	0	0
HYDRO-01 (kmol/h)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER (kmol/h)	45.787	0	0	0	45.787	0	129.787	0	0	2.79×10^{-7}	45.787	0	0	84.0
OXYGE-01 (kmol/h)	4.662	27.556	0	0	4.662	27.556	3.15×10^{-6}	0	0	4.662	4.662	27.556	0	0
FORMA-01 (kmol/h)	45.787	0	0	0	45.787	0	45.549	0	0	0.237	45.787	0	0	0
NITRO-01 (kmol/h)	103.664	103.664	0	0	103.664	103.664	4.25×10^{-5}	0	0	103.664	103.664	103.664	0	0
DIPHE-01 (kmol/h)	0	0	8.50	8.50	0	0	0	0	0	0	0	0	8.50	0
DIPHE-02 (kmol/h)	0	0	8.50	8.50	0	0	0	0	0	0	0	0	8.50	0
Total Flow (kmol/h)	200.364	131.220	17.0	17.0	200.364	131.220	175.80	46.25	46.25	108.564	200.364	177.470	17.0	84.0
Pressure (bar)	1.7	1.7	1	1	1.7	1	1.5	1	1	1.5	1.7	1.5	1	1.8
Vapor Frac	0.883	1	0	0	1	1	0	0.9143976	0	1	1	1	0	0
Liquid Frac	0.116	0	1	1	0	0	1	0.0856024	1	0	0	0	1	1
Solid Frac	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Density (mol/cc)	6.86×10^{-5}	5.59×10^{-5}	6.38×10^{-3}	5.30×10^{-3}	4.83×10^{-5}	4.03×10^{-5}	0.0415	3.90×10^{-5}	0.0234	1.05×10^{-4}	3.57×10^{-5}	5.43×10^{-5}	6.38×10^{-3}	0.0551
Average MW	26.290	28.850	162.211	162.211	26.290	28.850	21.164	32.042	32.042	28.189	26.290	29.682	162.211	18.015
Liq Vol 60F (L/min)	140.703	117.131	43.664	43.664	140.703	117.131	69.122	31.091	31.091	96.851	140.703	148.222	43.664	25.270

Table 3. Energy balance of Molybdenum-based process.

Stream ID	A2	AIR	DTHIN	DTHOUT	GH	INPUTAIR	LIQUID	METHANOL	METHIN	OFFGAS	PRODOUT	REACIN	TOTANK	WATER
From	ABSORBER	MIXER	HEATEX1	CONDENSR	EX2	COMP		MIXER	EX2		HEATEX1	REACTOR1	TANK	ABSORBER
To	EX2	COMP	TANK	HEATEX1	HEATEX1		ABSORBER	EX2		ABSORBER	REACTOR1	MIXER	CONDENSR	
Phase	MIXED	VAPOR	LIQUID	LIQUID	VAPOR	VAPOR	LIQUID	MIXED	LIQUID	VAPOR	VAPOR	VAPOR	LIQUID	LIQUID
Temperature (°C)	63.995	92.459	40	246.69	150	25	31.936	64.20	60	45.263	300	58.928	40	25
Pressure (bar)	1.7	1.7	1	1	1.7	1	1.5	1	1	1.5	1.7	1.5	1	1.8
Enthalpy (cal/mol)	−21,715.29	471.044	13,700.96	28,142.45	−19,910.51	-1.87×10^{-13}	−60,235.33	−48,290.74	−56,109.41	−950.7649	−18,685.22	−12,236.58	13,700.96	−68,262.2

Table 4. Material balance of silver-based process.

Stream ID	AIR	ERT	FORMALIN	LIQUID	METHANOL	OFFGAS	OUT1	REACIN	RECYCLE	TOABSRBR	WATER	WATER1	WATER2
From	MIXER	EX		HEATER	MIXER		DIS	REACTOR1	MIXER	ABSORBER	ABSORBER	EX	
To		REACTOR1	DIS	ABSORBER		ABSORBER	HEATER	MIXER	DIS	EX			EX
Phase	VAPOR	VAPOR	LIQUID	LIQUID	VAPOR	VAPOR	VAPOR	MIXED	LIQUID	VAPOR	LIQUID	LIQUID	MIXED
METHA-01 (kmol/h)	0	6.307	5.996	6.307	49.50	8.36×10^{-222}	6.307	49.810	0.310	6.307	0	0	0
HYDRO-01 (kmol/h)	0	14.943	2.17×10^{-8}	2.54×10^{-8}	0	14.943	2.54×10^{-8}	3.66×10^{-9}	3.66×10^{-9}	14.943	0	0	0
WATER (kmol/h)	0	35.617	110.56	117.617	0	3.73×10^{-6}	117.617	7.057	7.057	35.617	82.0	65.0	65.0
OXYGE-01 (kmol/h)	14.28	0	0	0	0	0	0	14.28	0	0	0	0	0
FORMA-01 (kmol/h)	0	46.728	42.850	46.075	0	0.652	46.075	3.225	3.225	46.728	0	0	0
NITRO-01 (kmol/h)	53.72	53.72	1.53×10^{-5}	1.74×10^{-5}	0	53.719	1.74×10^{-5}	53.72	2.09×10^{-6}	53.72	0	0	0
Total Flow (kmol/h)	68	157.315	159.407	170.0	49.50	69.31554	170.0	128.092	10.592	157.315	82.0	65.0	65.0
Pressure (bar)	1.8	1.8	0.5	1.5	1.1	1.5	1	1.2	0.5	1.8	1.8	1	1
Vapor Frac	1	1	0	0	1	1	1	0.933	0	1	0	0	0.967
Liquid Frac	0	0	1	1	0	0	0	0.066	1	0	1	1	0.032
Solid Frac	0	0	0	0	0	0	0	0	0	0	0	0	0
Density (mol/cc)	7.26×10^{-5}	2.48×10^{-5}	0.039	0.037	3.20×10^{-5}	9.63×10^{-5}	3.22×10^{-5}	4.65×10^{-5}	0.039	5.51×10^{-5}	0.055	0.055	3.33×10^{-5}
Average MW	28.850	24.039	21.771	21.791	32.042	22.427	21.791	29.524	22.083	24.039	18.015	18.015	18.015
Liq Vol 60F (L/min)	60.698	106.782	65.294	69.733	33.276	61.717	69.733	98.414	4.439	106.782	24.668	19.554	19.554

5.1.4. Energy Balance of Silver Oxide

The energy balance of the Molybdenum oxide process is shown in Table 5. The table shows the temperatures, pressures, and enthalpies of all the components of the process. The pressure varies from 0.5 bar to 1.8 bar during the process and temperature varies from 25 °C to 600 °C during the process. The inlet gas is at 25 °C, whereas the reactor has a temperature of 600 °C. The enthalpy in the reactor is −19,619.55 cal/mol. The highest pressure during the process is in the absorption column, which is 1.8 bar.

5.2. Catalyst Performance

The comparison of both catalytic processes' performance is given in Table 6. It can be observed that the size of the Molybdenum Oxide plant is larger due to the greater amount of air requirement, whereas the size of silver oxide plant is lesser.

5.3. Comparison of Molybdenum- and Silver-Based Processes

It can be observed from the results that the amount of methanol used was slightly different, but the amount of air varied significantly in the two processes. In the molybdenum oxide plant, the methanol was utilized at a rate of 46.25 kmol/h whereas it was utilized at a rate of 49.9 kmol/h in the silver-based plant. The amount of oxygen consumed in the silver-based plant was 27.56 kmol/h whereas the amount of oxygen required was at a rate of 15.12 kmol/h. Therefore, the lesser requirement oxygen in the silver-based plant lowers the utilities cost as well as decreasing the size of the equipment used. The capital cost in the case of silver is greater due to presence of an additional distillation column, however the size of overall plant is smaller though. The payback period of the silver-based plant is 2.8 years while it is 3.5 years for the molybdenum-based plant. The lesser payback period in the silver-based plant is due to a lower utility cost in the case of the silver-based process. The regeneration of silver catalyst is also possible. Therefore, from our results we can see that the silver plant has lower utility cost, shorter payback period, lower amount of oxygen required, and compact size as compared to molybdenum. Figures 3 and 4 show the comparison of the outcomes of the two processes for the formaldehyde formation i.e., Molybdenum-based and silver-based processes.

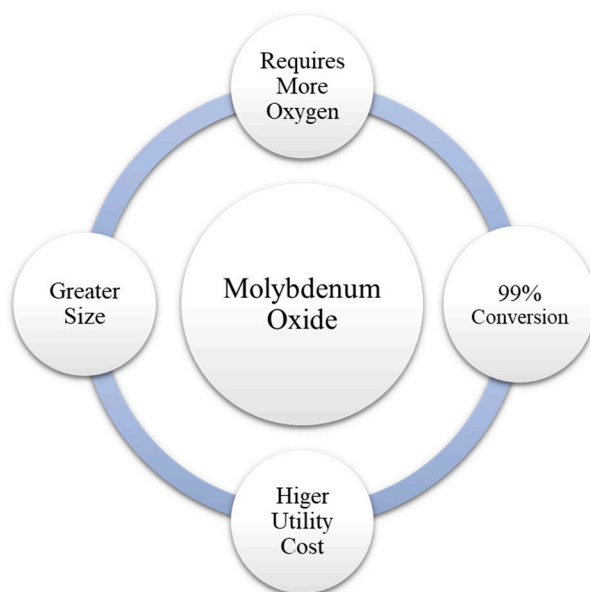


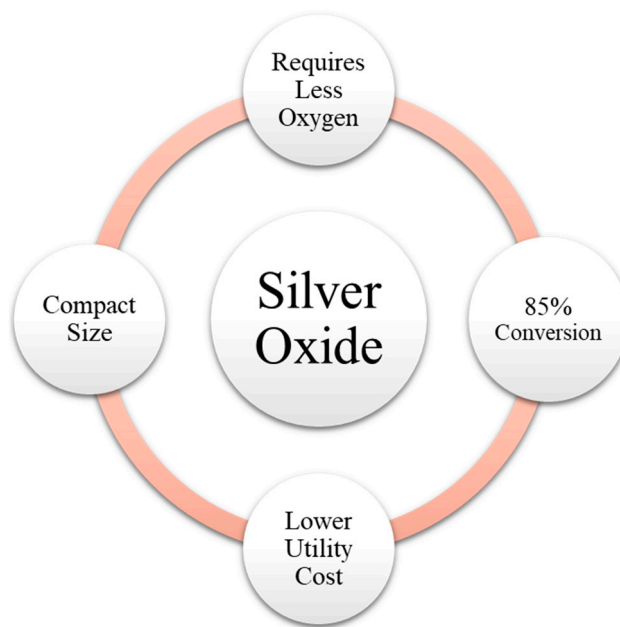
Figure 3. Molybdenum-based process.

Table 5. Energy balance of silver-based process.

Stream ID	AIR	ERT	FORMALIN	LIQUID	METHANOL	OFFGAS	OUT1	REACIN	RECYCLE	TOABSRBR	WATER	WATER1	WATER2
From	MIXER	EX		HEATER	MIXER		DIS	REACTOR1	MIXER	ABSORBER	ABSORBER	EX	
To		REACTOR1	DIS	ABSORBER		ABSORBER	HEATER	MIXER	DIS	EX			EX
Phase	VAPOR	VAPOR	LIQUID	LIQUID	VAPOR	VAPOR	VAPOR	MIXED	LIQUID	VAPOR	LIQUID	LIQUID	MIXED
Temperature (°C)	25	600	28.643	69.411	140	85.748	100	59.374	16.298	120	25	25	99.649
Pressure (bar)	1.8	1.8	0.5	1.5	1.1	1.5	1	1.2	0.5	1.8	1.8	1	1
Enthalpy (cal/mol)	-1.87×10^{-13}	−19,619.55	−59,483.02	−58,554.92	−46,668.7	−1078.707	−50,085.2	−22,892.57	−58,746	−24,078.11	−68,262.2	−68,262.2	−57,471.4

Table 6. Catalyst performance parameters.

Parameters	Molybdenum Oxide	Silver Oxide
Size	Larger	Compact
Capital Cost	\$6.2 M	\$7.1 M
Utility cost	\$2.3 M/Year	\$1.65 M/Year
Payback period	3.5 years	2.8 years

**Figure 4.** Silver oxide-based process.

6. Conclusions

The performance of two catalysts was studied simultaneously and the results were compared. The molybdenum-based plant has a larger plant size, high utility cost, but low cost of installation. Moreover, it has higher conversion of methanol to product i.e., 99%. The silver-based plant requires half the amount of air as compared to the molybdenum-based process, so it has compact plant size, the installation cost is high, but utility cost is low. However, the conversion is less in this process i.e., 75–85% as compared to the molybdenum-based process. Based on the comparative study and calculations, the silver-based process for formaldehyde production is better on an industrial scale.

Author Contributions: Conceptualization, S.R.N.; Data curation, K.S.; Formal analysis, S.A.A.T.; Funding acquisition, M.B.K.N.; Investigation, M.J.; Methodology, Y.M.; Project administration, S.R.N.; Software, S.A.A.T.; Supervision, S.R.N.; Validation, M.T.M.; Writing—Original draft, S.A.A.T., S.R.N.; Writing—review & editing, F.U., U.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors would like to acknowledge the National University of Sciences and Technology (NUST), Pakistan.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Webster, D.E.; Rouse, I.M. Production of Formaldehyde. U.S. Patent 4208353A, 17 June 1980.
2. Takashi, E.; Tamechika, Y.; Saburo, Y. Process for Preparing Formalin by Oxidation of Methanol. U.S. Patent 2908715A, 13 October 1959.
3. Meath, W.B. Production of Formaldehyde. U.S. Patent 2462413A, 22 February 1949.
4. Hall, J.L. Method for the Production of Formaldehyde. U.S. Patent 2384028A, 4 September 1945.

5. McClellan, W.R.; Stiles, A.B. Conversion of Methanol to Formaldehyde. U.S. Patent 3987107A, 19 October 1976.
6. Hoene, D.J. Formaldehyde Process. U.S. Patent 4343954A, 10 August 1982.
7. Hader, R.N.; Wallace, R.D.; McKinney, R.W. Formaldehyde from Methanol. *Ind. Eng. Chem.* **1952**, *44*, 1508–1518. [\[CrossRef\]](#)
8. Salthammer, T.; Mentese, S.; Marutzky, R. Formaldehyde in the Indoor Environment. *Chem. Rev.* **2010**, *110*, 2536–2572. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Tang, X.; Bai, Y.; Duong, A.; Smith, M.T.; Li, L.; Zhang, L. Formaldehyde in China: Production, consumption, exposure levels, and health effects. *Environ. Int.* **2009**, *35*, 1210–1224. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Abdollahi, M.; Hosseini, A. Formaldehyde. In *Encyclopedia of Toxicology*, 3rd ed.; Wexler, P., Ed.; Academic Press: Oxford, UK, 2014; pp. 653–656.
11. Dunky, M. Urea–formaldehyde (UF) adhesive resins for wood. *Int. J. Adhes. Adhes.* **1998**, *18*, 95–107. [\[CrossRef\]](#)
12. Dunky, M. Adhesives Based on Formaldehyde Condensation Resins. *Macromol. Symp.* **2004**, *217*, 417–430. [\[CrossRef\]](#)
13. Critical Review and Exergy Analysis of Formaldehyde Production Processes: Reviews in Chemical Engineering. 1 December 2014. Available online: <https://www.degruyter.com/view/j/revce.ahead-of-print/revce-2014-0022/revce-2014-0022.xml> (accessed on 26 April 2019).
14. Cheng, W.-H. Methanol and Formaldehyde Oxidation Study over Molybdenum Oxide. *J. Catal.* **1996**, *158*, 477–485. [\[CrossRef\]](#)
15. Adkins, H.; Peterson, W.R. The Oxidation of Methanol with Air Over Iron, Molybdenum, And Iron-Molybdenum Oxides. *J. Am. Chem. Soc.* **1931**, *53*, 1512–1520. [\[CrossRef\]](#)
16. Wachs, I.E.; Madix, R.J. The oxidation of methanol on a silver (110) catalyst. *Surf. Sci.* **1978**, *76*, 531–558. [\[CrossRef\]](#)
17. Brown, M.J.; Parkyns, N.D. Progress in the partial oxidation of methane to methanol and formaldehyde. *Catal. Today* **1991**, *8*, 305–335. [\[CrossRef\]](#)
18. Lefferts, L.; van Ommen, J.G.; Ross, J.R.H. The oxidative dehydrogenation of methanol to formaldehyde over silver catalysts in relation to the oxygen-silver interaction. *Appl. Catal.* **1986**, *23*, 385–402. [\[CrossRef\]](#)
19. Yang, T.-J.; Lunsford, J.H. Partial oxidation of methanol to formaldehyde over molybdenum oxide on silica. *J. Catal.* **1987**, *103*, 55–64. [\[CrossRef\]](#)
20. Qian, M.; Liauw, M.A.; Emig, G. Formaldehyde synthesis from methanol over silver catalysts. *Appl. Catal. Gen.* **2003**, *238*, 211–222. [\[CrossRef\]](#)
21. Waterhouse, G.I.N.; Bowmaker, G.A.; Metson, J.B. Influence of catalyst morphology on the performance of electrolytic silver catalysts for the partial oxidation of methanol to formaldehyde. *Appl. Catal. Gen.* **2004**, *266*, 257–273. [\[CrossRef\]](#)
22. Millar, G.J.; Collins, M. Industrial production of formaldehyde using polycrystalline silver catalyst. *Ind. Eng. Chem. Res.* **2017**, *56*, 9247–9265. [\[CrossRef\]](#)
23. Brenk, M. Silver Catalyst for Formaldehyde Preparation. U.S. Patent 8,471,071, 25 June 2013.
24. Heim, L.E.; Konnerth, H.; Prechtel, M.H. Future perspectives for formaldehyde: Pathways for reductive synthesis and energy storage. *Green Chem.* **2017**, *19*, 2347–2355. [\[CrossRef\]](#)

