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Implementation of Cleaner Production Principles in Formaldehyde Production

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ABSTRACT

Formaldehyde is the first of the series of aliphatic aldehydes. It is a basic chemical building block for the production of wide range of chemicals finding a wide variety of end uses. It can be manufactured by two different processes namely – dehydrogenation (Route – I) and oxidation (Route – II) process. First route being highly exothermic in nature, the removal of heat has to be done very effectively, where as the second route is endothermic in nature, addition of energy has to be done very effectively. Route – III, proposed in this paper, can be considered as more environmentally friendly route. Both the routes are carried out in a combined reactor. The total amount of energy require in this route for the production of formaldehyde is very low. Energy required from the external source for either removal or absorption of energy is ZERO. Approximately 50% of total energy and raw material requirement can be saved. Route – II is not an environmentally friendly, not a green reaction and green technology, but if it is coupled with Route – I, the scheme of reactions becomes a green reaction scheme. Thus full energy conservation is possible. Formaldehyde production by combined route is a good example in terms of energy conservation.

Keywords: **Cleaner production, energy conservation, formaldehyde, green reaction.**

1. INTRODUCTION:

Formaldehyde, HCHO, is the first of the series of aliphatic aldehydes. It was discovered 1859 and has been manufactured since the beginning of the twentieth century. At ordinary temperatures, pure formaldehyde is a colorless gas with a pungent, suffocating odor. Because of its relatively low cost, high purity, and variety of chemical reactions, formaldehyde has become one of the world's most important industrial and research chemicals. Formaldehyde is noted for its reactivity and its versatility as a chemical intermediate. It is used in the form of anhydrous monomer solutions, polymers, and derivatives. Formaldehyde is a basic chemical building block for the production of a wide range of chemicals finding a wide variety of end uses such as wood products, plastics, and coatings. Formaldehyde production according to use is: urea-formaldehyde resins, 24%; phenol–formaldehyde resins 16.5%; polyacetal resins, 13%; 1,4-butanediol (BDO), 11%; methylene diisocyanate (MDI), 7%; pentaerythritol, 5%; controlled release fertilizer, 3.5%; hexamethylenetetramine (HMTA), 3%; melamine–formaldehyde resins, 3%; miscellaneous, including chelating agents, trimethylolpropane, pyridine chemicals, nitro-paraffin derivatives, textile treating and trimethylolethane, 14%;. Formaldehyde is produced and sold as water solutions containing variable amounts of formaldehyde.

2. ROUTES AVAILABLE FOR PRODUCTION OF FORMALDEHYDE:

Being an important petrochemical, formaldehyde can be manufactured by two different processes namely – dehydrogenation and oxidation. Here in this paper, the process (oxidation and dehydrogenation) for manufacturing the product is considered separately as two different routes. The detailed discussion for the production of formaldehyde via these two routes is given as under:

Route – I

- **Scheme of reaction:**

Unit Process – Dehydrogenation

$$\underset{\text{Methanol}}{CH_3OH} \longrightarrow \underset{\text{Formaldehyde}}{HCHO} + H_2$$

Route – II

- **Scheme of reaction:**

Unit Process – Oxidation

$$\underset{\text{Methanol}}{CH_3OH} + \tfrac{1}{2}O_2 \longrightarrow \underset{\text{Formaldehyde}}{HCHO} + H_2O$$

2.1. Process Description:

Formldehyde can be manufactured from methanol by dehydrogenation and oxidation process. In dehydrogenation process, the temperature maintained is 600°C. the reaction is carried out in presence of oxides of ferrous & chromium. The reaction is highly endothermic in nature. Conversion is 70 – 80 % and the yield of the product is 99%. ($HCHO + H_2$) vapors absorbed in water & H_2 gets separated, hence 37% solution of HCHO so obtained called as "Formalin". Being highly energy intensive process, it requires large quantity of heating media. Unreacted methanol separated from formalin by distillation.

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In oxidation process, here the process is maintained at a temperature of 650°C. the reaction is carried out in presence of oxides of silver & molybdenum. The reaction is highly exothermic in nature. Conversion is 80 – 90 % and the yield of the product is 90%. Being highly energy intensive process, it requires large quantity of cooling water. Non – purified air, compressed to about 0.2 atm. gauge is preheated by heat exchange with reacting gases and then it is fed to methanol evaporator, where at high temperature condition methanol is evaporated. The ratio of CH_3OH to O_2 is maintained in the range of 30 – 50%, so that the required conditions are achieved. The mixed gases from evaporator are then heated in preheater and sent to a reactor where oxides of silver or molybdenum act as catalysts.

The activity of catalyst is controlled to maintain a balance between endothermic dehydrogenation and exothermic oxidation reactions at the reaction conditions of 450 – 650°C. Some complete combustion reaction takes place. The product gases are absorbed in a water scrubber which is cooled by external circulation and sent back to light end stripper. The bottom of stripper is then fed to alcohol fractionator where approximately 15% of unreacted methanol is recovered from top and is recycled. The bottom of fractionator contains product which is 37% solution of FORMALDEHYDE called as “Formalin”.

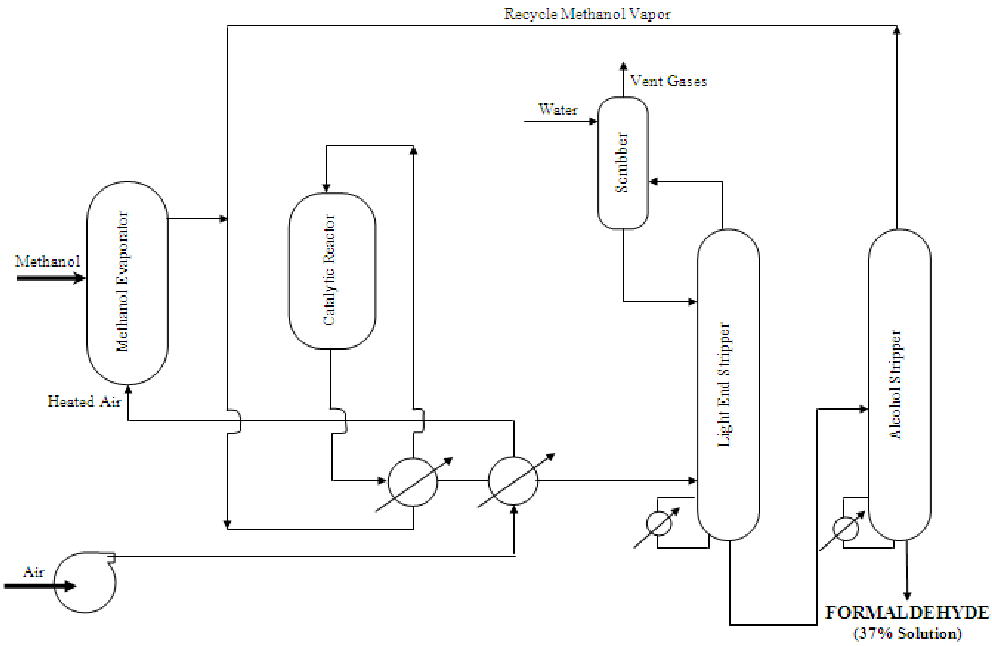

Figure: 1 Production of Formaldehyde from Methanol

3. THERMODYNAMIC CONSIDERATIONS:

<u>Route – I</u>

Estimation of Thermodynamic data:

Values of ΔH_R °(kJ / mole), ΔG°kJ / mole) and lnK at different temperatures in lnK are given by following equations:

$$\Delta H_R^{\circ} = 77910.7 + 29.47T + 0.015*T^2 - 3.27*10^{-6}*T^3 + 3.3*10^{-9}*T^4$$

$$\Delta G^{\circ} = 81358 - 95T + 0.005*T^2 - 8.1*10^{-7}*T^3 + 6.6*10^{-10}*T^4 \quad \ln k = 11.43 - \frac{9785.6}{T} + 6*10^{-4}*T + 9.7*10^{-8}*T^2 - 7.9*10^{-11}*T^3$$

<u>Route –II</u>

Estimation of Thermodynamic data:

Values of ΔH_R °(kJ / mole), ΔG°kJ / mole) and lnK at different temperatures in lnK are given by following equations:

$$\Delta H_R^{\circ} = -161216.5 + 20.51T - 0.0187*T^2 + 1.833*10^{-6}*T^3 + 1.813*10^{-9}*T^4$$

$$\Delta G^{\circ} = -159217 - 55.17T - 0.0063*T^2 + 4.83*10^{-7}*T^3 + 3.63*10^{-10}*T^4$$

$$\ln k = 6.63 - \frac{19150.5}{T} + 9.1*10^{-4}*T - 5.82*10^{-8}*T^2 - 4.37*10^{-11}*T^3$$

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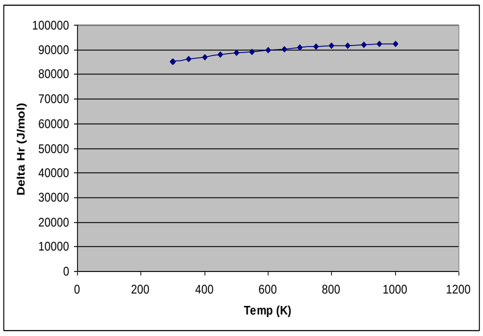
Based on the above set of equations, calculation of $\Delta H_R°$, $\Delta G°$and lnK is carried out for detailed thermodynamic analysis of each reaction involved in both routes in terms of feasibility of the reaction, nature of reaction. Also graphical behavior for individual reaction can also be plotted to determine the extent of reaction. From these equations the Values of $\Delta H_R°$, $\Delta G°$and lnK at different temperatures can be tabulated in Table: 1 as follows:

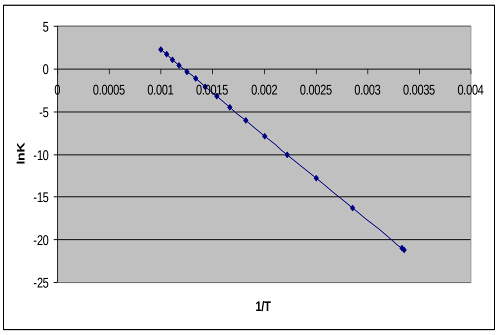
TABLE 1: Values of ΔH_R °(kJ / mole) and lnK at different temperatures for Route – I and Route – II

Temp (K)	Route – I (Dehydrogenation		Temp (K)	Route – II (Oxidation)	
	$\Delta H_R^°$	lnK		$\Delta H_R^°$	lnK
298	85300	-21.22	298	-156700	71.2
300	85340	-21	500	-155282	46.06
350	86297	-16.31	525	-155185	44.35
400	87175	-12.78	550	-155105	42.8
450	87974	-10.03	575	-155040	41.41
500	88697	-7.827	600	-154990	40.14
550	89345	-6.016	625	-154954	38.99
600	89922	-4.501	650	-154931	37.95
650	90431	-3.215	675	-154922	37
700	90876	-2.109	700	-154924	36.14
750	91262	-1.146	725	-154938	35.36
800	91592	-0.3	750	-154964	34.64
850	91874	0.4491	775	-154999	34
900	92111	1.1181	800	-155044	33.41
950	92312	1.7192	--	--	--
1000	92482	2.2624	--	--	--

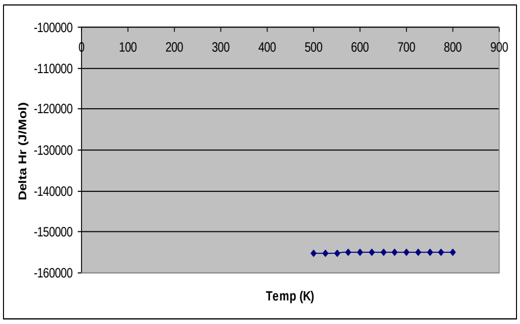
On the basis of the data tabulated in Table: 1, following are the graphs between $\Delta H_R°$□versus Temperature and lnK versus 1 / T obtained as under:

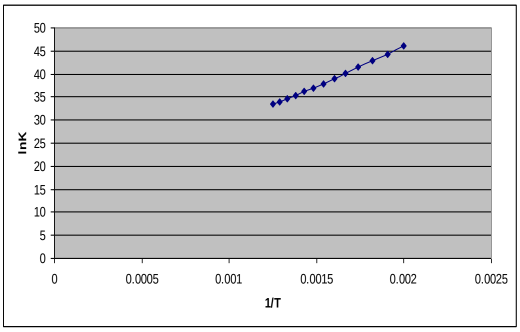
For Route – I: Unit Process – Dehydrogenation





For Route – II: Unit Process – Oxidation





3.1. Critical Thermodynamic Analysis of FORMALDEHYDE for three routes under considerations.

For Route – I: Unit Process - Dehydrogenation

Dehydrogenation reaction is highly endothermic in nature having heat of reaction value in the range of 85 to 93 KJ /

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mol of Methanol. The values of "lnK" ranges from -21.0 to 2.0. It indicates that reaction is highly reversible, so stringent control measures are required. The values of lnK are very low; practically *zero* up to 700 K. Being highly energy intensive process, it requires large quantity of heating media. Conversion is 80% and yield is above 99%. The value of conversion level can be increased at high temperature i.e. beyond 900 K. This happens to be an environmentally friendly route as O_2 (from air) is not required & has higher yield.

For Route – II: Unit Process - Oxidation
Oxidation reaction is very highly exothermic in nature having the heat of reaction value in the range of -155 to -156 KJ / mol of Methanol. The value of "lnK" ranges from 33.0 to 71.0. It indicates that reaction is highly irreversible, highly feasible and conversion level obtained can be of the order of 90%. The yield of the product is also 90%. Thus there is a full scope to increase the actual conversion levels and raw material requirements can be reduced. Stringent air pollution control measures are required. Being highly energy intensive process, large quantity of cooling media is required. The reaction is irreversible and it is a most favorable reaction for cleaner production implementation.

For Route – III: Combined Route – This route is based on the principles of carrying out dehydrogenation and oxidation reactions simultaneously using methanol as a raw material.

In this investigation, as the new technological option, Route – I being endothermic and Route – II being exothermic, combined reactor will give maximum benefits carrying both reactions (dehydrogenation and oxidation) simultaneously; the route can be converted to environmentally friendly route. Route – II is not an environmentally friendly, not a green reaction and not a green technology. However, if it couples with Route – I becomes a green reaction scheme. Conversion in dehydrogenation reaction and oxidation reaction is 80% and 90% respectively. This combined route will provide the most suitable conditions for eco – efficient environment. Route – III seems to be more environmentally friendly and more energy efficient route. Thus, it seems to be a most favorable route for cleaner production implementation.

3.2. Conclusion based on thermodynamics:

Thus, all the two reactions under considerations, first reaction being highly exothermic in nature, the removal of heat have to be done very effectively, where as the second reaction is endothermic in nature, addition of energy has to be done very effectively. The relevant material balance and energy balance flow sheet can be prepared based on actual plant capacity data.

The data tabulated in above tables is expected to be very useful while implementing energy conservation in plant manufacturing formaldehyde. Dehydrogenation being endothermic in nature, it requires large amount of energy in terms of heating media and oxidation reaction is highly exothermic in nature, it requires large amount of energy in terms of cooling media. In other words, both the routes are highly energy intensive. If both Routes – (I) & (II) are combined i. e. oxidation process as well as dehydrogenation process occur simultaneously using shell and tube heat exchanger as a reactor, then heat evolved on tube side wherein oxidation reaction is being carried out can be utilized conveniently to heat the entire mass from shell side where dehydrogenation reaction is being carried out. Thus full energy conservation can be achieved. Energy requirements – cooling media for Route – (II) as well as heating media for Route – (I) reduces to zero. According to energy balance flow data, energy requirement from external source for this combined route is zero. Thus for the implementation of Cleaner Production principles, thermodynamics aspects are of utmost importance. Finally it can be summarized that Formaldehyde production by combined route i. e Route – III is a good example of cleaner production principles.

4. ANALYSIS OF TECHNOLOGIES FROM CLEANER PRODUCTION POINT OF VIEW:

In Route – I, formaldehyde is produced by the dehydrogenation of methanol which would produce anhydrous or highly concentrated formaldehyde solutions. In dehydrogenation process, the temperature maintained is 600°C and the reaction is carried out in presence of oxides of ferrous & chromium. Fresh methanol with recycled quantity of methanol is fed to the reactor operated at 600°C and 1 atmospheric pressure to produce formaldehyde. The reaction is highly endothermic in nature. Conversion is 70 – 80 % and the yield of the product is 99%. ($HCHO$ + H_2) vapors absorbed in water & H_2 gets separated, hence 37% solution of HCHO so obtained called as "Formalin". Being highly energy intensive process, it requires large quantity of heating media. Unreacted methanol separated from formalin by distillation. Route-I happens to be environmentally friendly route as O_2 (from air) not required and has higher yield than Route-II.

In Route – II, formaldehyde is produced by the oxidation of methanol which would produce anhydrous or highly concentrated formaldehyde solutions. Methanol was oxidized over a copper catalyst, but this has been almost completely replaced with silver. The silver-catalyzed reactions occur at essentially atmospheric pressure and 600 to 650°C. The reaction is highly exothermic (-156 KJ /mol) in nature. Conversion is 80-90% and yield is 90%. The mixture passes through a super heater to a catalyst bed of silver crystals or layers of silver gauze. The product is then rapidly cooled in a steam generator and then in water cooled heat exchanger and fed to the bottom of an absorption tower. Absorber bottoms go to a distillation tower where methanol is recovered for recycle to the reactor. The base stream from distillation, an aqueous solution of formaldehyde, is usually sent to an anion exchange unit which reduces the formic acid to specification level. HCHO vapors absorbed in H2O and one obtains 37% solution of HCHO called as Formalin. The product contains up to 55% formaldehyde

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and less than 1.5% methanol. The reaction occurs at essentially adiabatic conditions. Recycled methanol required for a 50–55% product is 0.25–0.50 parts per part of fresh methanol. With increasing energy costs, maximum methanol conversion is desirable, eliminating the need for the energy-intensive distillation for methanol recovery. In another process, tail gas from the absorber is recycled to the reactor. This process can produce 50% formaldehyde with about 1.0% methanol without a distillation tower. Methanol recovery can be obviated in two-stage oxidation systems where, for example, part of the methanol is converted with a silver catalyst, the product is cooled, excess air is added, and the remaining methanol is converted over a metal oxide catalyst such as that described below. In another two-stage process, both first and second stages use silver catalysts. Formaldehyde–methanol solutions can be made directly from methanol oxidation product by absorption in methanol. Aqueous formaldehyde is corrosive to carbon steel, but formaldehyde in the vapor phase is not. All parts of the manufacturing equipment exposed to hot formaldehyde solutions must be a corrosion-resistant alloy such as type-316 stainless steel. Theoretically, equipment can be of carbon steel, but in practice alloys are required in this part of the plant to protect the sensitive silver catalyst from metal contamination. Water is also generated along with the product. Being highly energy intensive process, it requires large amount of cooling media (water). This route produces air emissions such as Nox, CO etc. Hence stringent air pollution control measures required.

5. MATERIAL BALANCE AND ENERGY BALANCE FOR FORMALDEHYDE PRODUCTION:

5.1 Material Balance for <u>Formaldehyde</u>
Production for *Route – I, II & III*:

Basis: 50 TPD (1666.7 kgmoles/day) of Formaldehyde produced

Unit: kgmoles/day

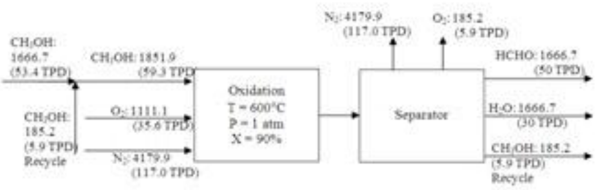

Figure: 2 Material Balance diagram for Formaldehyde Production (Route – I)

Route – III suggested in this investigation appears to be more attractive and more environmentally than Route – I and Route - II. This new technological option is considered as a combined route, in which both the reactions are carried out simultaneously. If both is processes are combined i. e. oxidation reaction as well as dehydrogenation reaction occur simultaneously using shell and tube heat exchanger as a reactor, then heat evolved on tube side wherein oxidation reaction is being carried out can be utilized conveniently to heat the entire mass from shell side wherein dehydrogenation reaction is being carried out. Thus, full energy conservation can be achieved. Energy requirements in terms of heating media for route-I as well as cooling media for route-II reduces to zero. Energy evolved in oxidation process due to high exothermic reaction is fully utilized in dehydrogenation as if the reaction is highly endothermic in nature. By this option sufficient amount of energy can be saved and energy costing by thus can be reduced. Hence, this combined route can be considered to be very cost effective. Based on material balances and energy balances data, energy requirement from external source for the combined route is, thus, zero. Temperature of reaction being very high of the order of 600-650oC, some quantity of nitrogen from air is likely to get oxidized to NOx. Thus, quantity of gaseous stream coming out of plant containing pollutants gets reduced considerably by 65%. Thus, intensity of air pollution gets reduced by a factor of three. Thus, combined route is likely to be highly energy efficient and more environmentally friendly route.

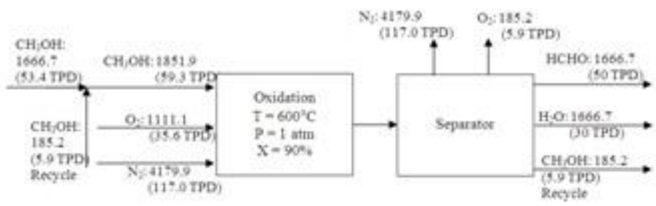

Figure: 3 Material Balance diagram for Formaldehyde Production (Route – II)

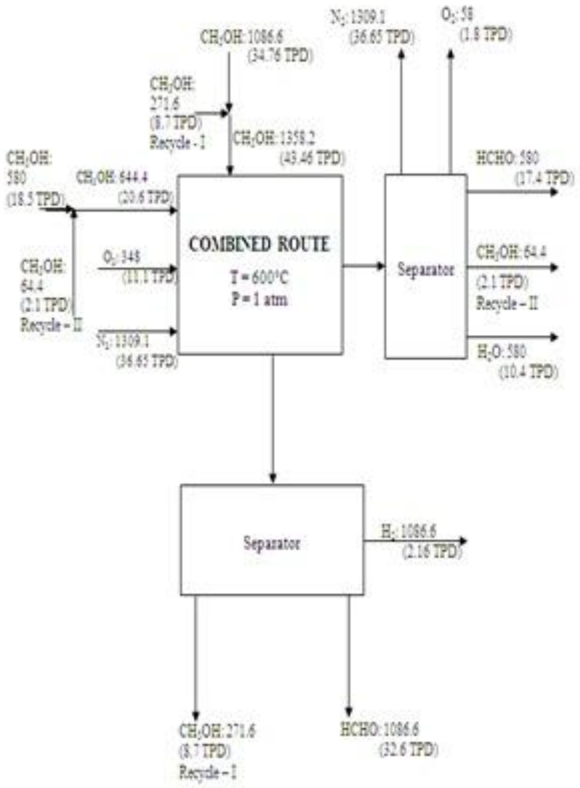

Figure: 4 Material Balance diagram for Formaldehyde Production (Route – III)

5.2 Comparison of TWO routes based on Material Balance Principles

Finally we can summarize the above two routes in common table by material balance principles for the production of 50 TPD of formaldehyde as under:

TABLE 2: Comparison of THREE routes based on Material Balance Principles

	Dehydrogenation route	Oxidation route	Combined route
CH_3OH required	66.66 TPD	59.3 TPD	64.06 TPD
Oxygen required	--	35.6 TPD	11.1 TPD
Air required	--	152.6 TPD	47.7 TPD

From the above table, it could be seen that formaldehyde production by combined route is a good example of in terms of waste minimization and energy Conservation and also it is taken as an eco – friendly route.

5.3 Energy Balance for Formaldehyde Production for *Route – I, II & III*:

Basis: 50 TPD (1666.7 kgmoles/day) of Formaldehyde produced

Unit: kJ/day

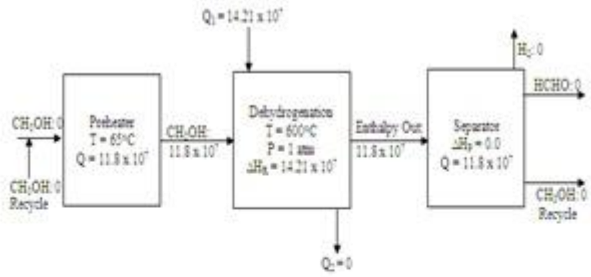

Figure: 5 Energy Balance diagram for Formaldehyde Production (Route – I)

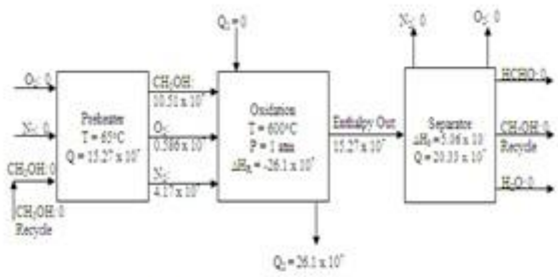

Figure: 6 Energy Balance diagram for Formaldehyde Production (Route – II)

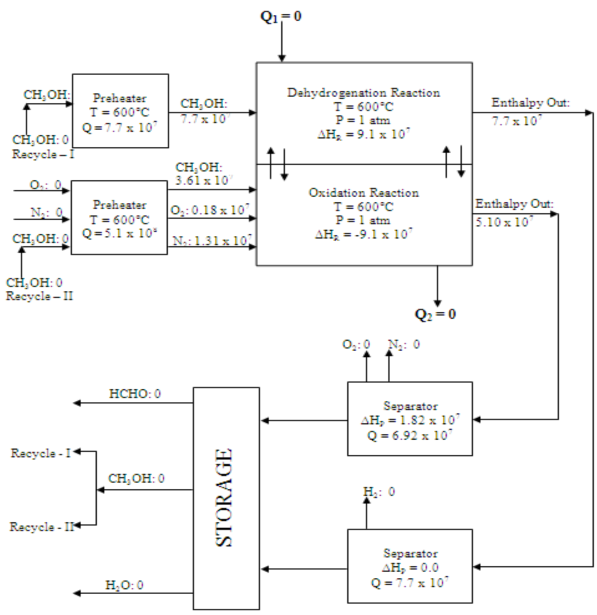

Figure: 7 Energy Balance diagram for Formaldehyde Production (Route – III)

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5.4. Comparison of THREE routes based on Energy Balance Principles:

The Energy requirement for entire three routes for the production of formaldehyde can be summarized with respect to energy balance in a common table as under:

TABLE 3: Comparison of THREE routes based on Energy Balance Principles

	Preheating (kJ / day)	**Heat to be absorbed / removed (kJ / day)**	**Separation (kJ / day)**	**TOTAL (kJ / day)**
Route – I	11.8 x 10^7	14.21 x 10^7	11.8 x 10^7	**37.81 x 10^7**
Route – II	15.27 x 10^7	26.1 x 10^7	20.33 x 10^7	**61.7 x 10^7**
Route – III	12.8 x 10^7	**0.0**	14.62 x 10^7	**27.42 x 10^7**

From the above comparison, it is seen that among three routes total energy requirement (kJ / day) in terms of preheating the raw materials and separation of products from other chemical spices in combined route (Route – III) is very low in comparison with the other two routes. In other words, Dehydrogenation route (since it is not so commonly used) requires total energy 37.81 x 10^7 kJ / day, whereas combined route requires total energy of 27.42 x 10^7 kJ / day. Hence in this combined route (Route – III) approximately 27 – 28% of total energy can be saved. This is the good example of energy conservation. In comparison to Route – II (most commonly used process) and Route – III, it is seen from the data tabulated above, the total energy required in Route – II is 61.7 x 10^7 kJ / day, whereas Route - III requires total energy of 27.42 x 10^7 kJ / day. Hence in this combined route (Route – III) approximately 45% of total energy can be saved. So, this combined route can also become the best example of energy conservation. As a result, this route is considered as the new technological option, in case of good energy conservation and waste minimization, for the formaldehyde production. Furthermore it requires **no (zero) energy** (as the energy evolved during oxidation reaction is fully absorbed by dehydrogenation reaction) from external source in either terms of heating or cooling media. Thus, good energy conservation can be achieved by this option. So, combined route can be considered as most energy efficient and more eco – friendly route. "Utilizing Combined Route" for the production of Formaldehyde is a good example of **"Cleaner Production".**

6. CONCLUSION:

From the above discussion and analysis, formaldehyde is an important and well known petrochemical manufactured by many renowned chemical industries. As discussed earlier, this petrochemical can be manufactured by two different processes namely – dehydrogenation and oxidation.

Route – I refers to dehydrogenation reaction, basically endothermic in nature. So this process requires large amount of heating media. Thus the process becomes highly intensive in nature. Critical analysis of material and energy balance states that, for the production of 50 TPD of formaldehyde, the total quantity of methanol required to feed into reactor is 66.66 TPD. Also co – product hydrogen 3.33 TPD is coming out with the main product formaldehyde. ($HCHO + H_2$) vapors absorbed in water & H2 gets separated, hence 37% solution of HCHO so obtained called as "Formalin". Route-I happens to be environmentally friendly route as it does not require O_2 (from air) and has higher yield than Route-II. The total amount of energy require in this route for the production of formaldehyde is 37.81 x 107 kJ / day. Production of formaldehyde is by the dehydrogenation of methanol which would produce anhydrous or highly concentrated formaldehyde solutions. For some formaldehyde users, minimization of the water in the feed reduces energy costs, effluent generation, and losses while providing more desirable reaction conditions.

Route – II, most of the world's commercial formaldehyde is manufactured from methanol and air either by a process using a silver catalyst or one using a metal oxide catalyst refers to oxidation reaction, basically exothermic in nature. So this process requires large amount of cooling media. Thus the process becomes highly intensive in nature. Critical analysis of material and energy balance states that, for the production of 50 TPD of formaldehyde, the total quantity of methanol required to feed into reactor is 59.3 TPD. The quantity of air used is 152.6 TPD containing 35.6 TPD of oxygen as an oxidizing agent and nitrogen 117 TPD as an inert. The total amount of energy require in this route for the production of formaldehyde is 61.7 x 107 kJ / day. Generation of water is 30 TPD for this route. Compared this situation with Route – I more energy and raw material is required in this route. Route-II not happens to be environmentally friendly route, as it produces air emissions such as NOx, CO etc. Hence stringent air pollution control measures required.

Route – III, in this investigation, can be considered as more environmentally friendly route. As the new technological option, both the routes are carried out in a combined reactor. The total amount of energy require in this route for the production of formaldehyde is 27.42 x 107 kJ / day. Energy required from the external source for either removal or absorption of energy is **ZERO**. It is seen that among three routes total energy requirement in terms of preheating the raw materials and separation of products in combined route is very low in comparison with the other two routes. Hence, compared with Route – II approximately 50% of total energy can be saved. Also raw material requirement in this route can also be reduced significantly. Route – II is not an environmentally friendly, not a green reaction and not a green technology. However, if it couples with Route – I becomes a green reaction scheme. Thus full energy conservation can be achieved. Energy requirements, cooling media for Route – (I) as well as heating media for Route – (II) reduces to zero. Thus, quantity of gaseous stream coming out of plant containing pollutants gets reduced considerably by 65%. Thus, intensity of air pollution gets reduced by a factor of three. Finally it can be summarized that formaldehyde production by combined route is a good example in terms of energy conservation for the implementation of cleaner production principles.

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