

Exothermic reactions Runway for Pressure Reaction: Catalytic Hydrogenation of Schiff Base in Pilot Autoclave

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Abstract:- Exothermic reactions with runaway potentials are carried out in industry either in continuous or semi-batch mode. In non-pressure reaction controlled reactant is fed to the reactor at predetermined rate continuously irrespective of reaction conditions and it is likely that rate of addition of the controlled reactant is more. This will lead to accumulation of this reactant in the reaction mass which at latter stage will react at faster rate due to higher temperature, leading to runaway reaction. Catalytic hydrogenation of Schiff Base Dibenzal Ethylene diamine to Dibenzyl Ethylene diamine, theoretical Estimation of ΔH_r from bond energies and practical determination of ΔH_r by its removal as given in equation (iv) is carried out. The gas chromatograms of product samples were carried out to check extent of reaction. The theoretical ΔH_r was confirmed with experimental ΔH_r by autoclave avoiding loss of heat to reactor or atmosphere on plant scale. Practical determination of ΔH_r by removing the heat, Q , and measuring the same at nearly at constant process temperature and also from heat transfer coefficient, U , for the system.

Keywords:- Exothermic Reaction, Temperature Runway, Non Pressure Reaction, Hydrogenation of Schiff Base

1. Introduction

In process industry, raw materials are converted into various commercial products using different techniques. One frequently used method is their conversion by exothermic chemical reactions which can lead to a reactor thermal runaway if the heat generation rate exceeds the heat removal rate during process [1]. Pressure build-up during the runaway is caused by an increasing vapor pressure of liquid components and by the production of noncondensable gases. Apart from the loss of reactor inventory due to an uncontrolled conversion process, a runaway reaction may lead to severely damaged equipment or even a physical explosion if pressure build-up inside the reactor exceeds the design pressure. The emergency relief system is composed of vent area, vent rupture membrane, safety relief valve, vent pipes, blow down tank, horizontal condenser, scrubber with absorber and vertical condenser, outflow chimney, corresponding pumps, fan, pipes, fitting, and supply system with electricity, cooling water, and neutralization medium. In case of reaction runaway, the vent rupture disc opens and the reactor mixture blows out into the vent pipes and flows into blow down tank. Due to short residence time of reactor mixture in the blow down tank, the volume changes and the pressure decreases at isothermal conditions, which results in the condensation of reaction mixtures. A high pressure reaction vessel is a chemical reaction vessel that can conduct a reaction under elevated pressure (i.e., greater than atmospheric pressure). This pressure can be caused by the reaction itself or from reactants added to the vessel. These vessels can offer a multitude of advantages over a conventional round bottom flask reaction. The present work to arrive at reasonably close prediction and prevention of runaway reactions carried out by and within means of MSME chemical units consists of theoretical estimation of ΔH_r to predict the runaway nature of reaction and its comparison with practically determined ΔH_r and details measures to prevent a potentially runaway reaction. In semi-batch mode reactions carried out in MSME units, one of the reactant is control fed to the reactor over a period and the heat generated is also removed continuously to prevent built up of heat leading to runaway reaction. Majority of chemical reactions carried out in industry are exothermic in nature. Some reactions require very little activation energy to be initiated. If the reaction is exothermic, the energy initially produced may accelerate a continued reaction and release energy too rapidly to be controlled.. The autoclave reactor is a small cylindrical reactor; built to withstand high pressures, used to evaluate the kinetics of high-temperature, high-pressure reactions and the production of small quantities of specialty chemicals. The reactor is typically packed with a supported catalyst, and reactant is added by

injection. Pressure in the system is elevated by increasing the temperature of the autoclave. Additional pressure, if needed, can be obtained with the injection of additional gaseous reactant or an inert.

While studying exothermic reactions for potential runaway, none of the two methods, theoretical estimation or experimental determination of Heat of Reaction, ΔH_r , give accurate results as mentioned earlier. Since process design in exothermic reactions is advisable to be carried out with 25 % safety margin, theoretical estimation results within 25 % of actually observed on plant scale should be acceptable. Non pressure reaction are controlled reactant is fed to the reactor at predetermined rate continuously irrespective of reaction conditions and it is likely that rate of addition of the controlled reactant is more than consumption in reaction due to deviation in reaction condition parameters. This will lead to accumulation of this reactant in the reaction mass which at latter stage will react at faster rate due to higher temperature, leading to runaway reaction.

The exothermic chemical reactions carried out in MSME industry are semi batch processes wherein one of the reactant is control fed to the reactor over reaction period so as to control heat of reaction in progressive manner that can be removed by cooling system over a period. In continuous mode, all reactants are fed to the reactor continuously and the process is equilibrated with intrinsic design to control the flow through the reactor to avoid runaway and the product removed continuously. These type of reactions are carried out in large scale industry and are not within the scope of present study. Reactions carried out in MSME units are usually known and prediction of thermal runaway can be made by evaluating thermal kinetics of the reaction theoretically. Heat removal capacity of cooling system can be calculated with detailed engineering and cooling system data or with simple experiment. Case study of Schiff Base catalytic hydrogenation in autoclave is presented here..

2. Estimation of Accumulation of Controlled Reactant

The exothermic chemical reactions carried out in industry are semi batch processes wherein one of the reactant is control fed to the reactor over reaction period so as to control heat of reaction in progressive manner that can be removed by cooling system over a period. Here it is important that the rate of reaction, and therefore rate of heat generation is equivalent to rate of addition of controlled reactant. If the rate of addition of controlled reactant is more than the rate of reaction, the excess of controlled reactant will accumulate in reaction mass and at one stage the rate of reaction will increase causing all of this accumulated reactant to react in a very short time. This will result in large heat generation in short time and the existing cooling system will not be able to remove this heat in equivalent time leading to runaway reaction. It is, therefore, important to determine the rate of addition of controlled reactant so that no accumulation of controlled reactant in reaction mass takes place. This can be done in lab experiments by analyzing the reaction mass for controlled reactant. These semi-batch reactions can be classified in two types.

2.1. Pressure Reactions

In this type, the reaction is carried out under pressure in pressure vessel, autoclave, and controlled reactant is also fed under pressure. In this type, if the heat generated is more than removed, pressure in the reactor will increase and will prevent flow of controlled reactant to the reactor preventing accumulation of reactant in the reaction mass. The exotherm due to sudden reaction of accumulated reactant and, therefore, runaway is thus prevented. These reactions are comparatively less prone to runaway even as pressure hazards are present.

2.2. Non-Pressure Reactions

In this type, the controlled reactant is fed to the reactor at predetermined rate continuously irrespective of reaction conditions and it is likely that rate of addition of the controlled reactant is more than consumption in reaction due to deviation in reaction condition parameters. This will lead to accumulation of this reactant in the reaction mass which at latter stage will react at faster rate due to higher temperature, leading to runaway reaction.

3. Material

3.1 Schiff base

The term Schiff base is normally applied to these compounds when they are being used as ligands to form coordination complexes with metal ions. Such complexes occur naturally, for instance in corrin, but the majority of Schiff bases are artificial and are used to form many important catalysts, such as Jacobsen's catalyst. a Schiff base (named after Hugo Schiff) is a compound with the general structure $R_1R_2C=NR_3$ (R_3 = alkyl or aryl, but not hydrogen). They can be considered a sub-class of imines, being either secondary ketimines or secondary aldimines depending on their structure. The term is often synonymous with azomethine which refers specifically to secondary aldimines (i.e. $R-CH=NR'$ where R'

≠ H). The Schiff base used for the present study was Dibenzal Ethylenediamine having formula $\text{PhCH}_2\text{CH}=\text{NCH}_2\text{CH}_2\text{N}=\text{CHCH}_2\text{Ph}$ and molar mass 236.31 g/Mole.

3.2. Dibenzyl Ethylenediamine

Dibenzyl Ethylenediamine $\text{C}_{20}\text{H}_{16}\text{N}_2$ is an organic compound with formula $\text{PhCH}_2\text{CHNHCH}_2\text{CH}_2\text{NHCHCH}_2\text{Ph}$, where Ph is Phenyl, C_6H_5 , with molar mass 240.34 g/Mole and Melting Point 26°C .

3.3. AutoClave

An autoclave is a machine used to carry out industrial and scientific processes requiring elevated temperature and pressure in relation to ambient pressure and/or temperature. Autoclaves are used in the chemical industry to cure coatings and vulcanize rubber and for hydrothermal synthesis. Industrial autoclaves are used in industrial applications, especially in the manufacturing of composites. Many autoclaves are used to pressurized saturated steam at 121°C (250°F). Hydrogenation of Schiff Base Dibenzal Ethylene diamine to Dibenzyl Ethylene diamine was carried out in 2.0 litre capacity pilot Stainless Steel 316 autoclave. The autoclave was provided with insulated external electric heating, agitator and cooling coil inside the vessel. Temperature probes to measure temperatures inside the vessel and of inlet and outlet cooling water from the coil were also provided. The vessel was fitted with pressure gauge, safety release valve and inlet hydrogen gas piping.

3.4. Catalyst

The catalyst used for hydrogenation was 10% platinum metal catalyst.

4. Methodology

The following quantities of Schiff Base and solvent along with catalyst were charged into the autoclave. The depth of the cooling coil dipping in the reaction mass was noted to calculate cooling area and autoclave securely closed. Reaction mass was heated to the desired process temperature, with cooling and agitation on. Cooling water flow rate was measured by collecting the cooling water in measuring container. Once the reaction mass, cooling water inlet and outlet temperatures are stabilized, the air inside the vessel was displaced with nitrogen gas and then the nitrogen was displaced with hydrogen gas. The hydrogen gas pressure was maintained at desired level by adjusting gas inlet valve and reaction continued at stabilized temperatures. After most of the reaction was complete, the temperature of reaction mass dropped and at one point hydrogen gas absorption stopped signaling completion of reaction.



Figure 1:- Autoclave Setup

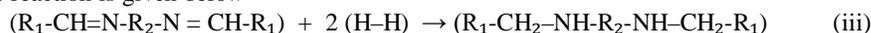
5. Therotical Calculation of ΔHr

Hydrogenation of Schiff Base Dibenzal Ethylene diamine to Dibenzyl Ethylene diamine

Theoretical Estimation of ΔHr from bond energies (Method 1).

Bond Energies from chem.libretexts.

The reaction is given below



Where R_1 is C_6H_5 and R_2 is CH_2CH_2 , and reaction mass is 240.

In this reaction, bonds broken are 2 C = N bonds (Bond energy 615 KJ/M) and 2 H – H bonds (Bond energy 432 KJ/M). Bonds formed are 2 C – H bonds (Bond energy 413 KJ/M), 2 C – N bonds (Bond energy 305 KJ/M) and 2 N – H bonds (Bond energy 391 KJ/M)

Therefore, $\Delta H_r = 2*(615+432) - 2*(413 + 305 + 391) = -124 \text{ KJ/M} = -29.636 \text{ KCal/M}$

That is 29636 Calories of heat will be released in formation of 240 g. of reaction mass. Assuming C_p , Specific heat capacity, common for organic compounds, at 2 joules/gm or 0.478 Cal / g., this will increase temperature of the reaction mass in adiabatic condition, ΔT_{ad} , to $\Delta T_{ad} = 29636/(240 * 0.478) = 258.3^\circ\text{C}$ which is above 200°C and the reaction in the absence of heat removal will be runaway reaction.

6. Practical Determination of ΔH_r

6.1 Method 1: Measuring ΔT_{ad}

Measuring increase in temperature with no loss of heat by following equation

$$\Delta T_{ad} = -\Delta H_r / C_p \quad \text{or} \quad -\Delta H_r = \Delta T_{ad} * C_p \quad (iii)$$

C_p is specific heat capacity of reaction mass. C_p can be calculated from values of reaction components available from data banks. If not available, it can be assumed 2.0 joules / g for organic compounds. ΔT_{ad} to be determined in lab experiment ensuring that no heat is lost except for increasing temperature of reaction mass.

6.2. Method 2: From measuring by removal

- ΔH_r can also be determined by carrying out reaction at desired temperature and removing the generated ΔH_r by cooling medium and measuring the heat removed from following equation

$$-\Delta H_r = m * (T_2 - T_1) * C_{pc} \quad (iv)$$

Where,

'm' is mass of the cooling medium and $(T_2 - T_1)$ is increase in cooling medium temperature i.e. outlet temperature T_2 minus inlet temperature T_1 of cooling medium from the cooling system such as coil or jacket and ' C_{pc} ' is specific heat capacity of cooling medium.

- Alternatively ΔH_r can be determined as heat removed, Q, from heat transfer coefficient U, of the system from following formula

$$U = Q / (A * \Delta T_{lm}), \quad (v)$$

$$\text{or } Q = U * A * \Delta T_{lm},$$

(Va) where

U is overall heat transfer coefficient in Cal/ (M²Sec⁰C)

Q is heat removed at constant reaction temperature, T⁰C, in Cal/Sec

A is area of the cooling system in M² and ΔT_{lm} is Log Mean Temperature Difference (LMTD) given as

$$\Delta T_{lm} = ((T-T_1) - (T-T_2)) / \ln((T-T_1) / (T-T_2)), ^\circ\text{C}.$$

$\Delta H_r = Q * t$, (Vb) t is reaction period in Seconds.

6.3. Practical Difficulties

Even as both these methods appear good enough for the measurement of ΔH_r , practically it is very difficult to prevent loss of heat except to heat the reaction mass. Significant heat is lost for heating the reaction equipment mass. This is known as ϕ factor and is explained below. In addition, heat is also lost to atmosphere due to imperfect insulation in lab scale experiments. Also in method 2 of ΔH_r determination by cooling medium, it is not possible to maintain desired temperature throughout the reaction because as the rate of reaction will slow down, the reaction temperature will come down with steady state cooling and so also reactor mass temperature. This means heat is also removed from reactor mass an addition to from reaction mass. Such conditions will lead to wrong estimations of ΔH_r .

Φ Factor:

The heat generated in an exothermic reaction is consumed in three ways.

- To raise the temperature of reaction mass
- To raise the temperature of the reactor and
- Heat loss to the atmosphere

Φ factor is correlation of heat consumed to raise the temperature of reactor and is given as

$$\Phi = 1 + (\text{Mass of reactor} \times \text{heat capacity of reactor}) / (\text{Reaction Mass} \times \text{heat capacity of reaction mass})$$

In large scale equipment, the φ factor of a vessel during a runaway will be close to unity because the thermal mass of the reactor will be low compared to thermal mass of the reaction mixture. In lab scale or pilot scale equipment, however, this φ factor is significantly higher than 1. Similarly, whereas it takes about 20 minutes to drop temperature by 1°C at 80°C in a 2000 litre reactor, it takes only about 10 seconds for the same drop in 10 ml test tube because of loss of heat to atmosphere. This higher loss of heat to atmosphere at lab scale will also affect true determination of ΔHr. For near accurate experimental results, this φ factor should be 1 and there should be no loss of reaction heat to atmosphere. This is possible in a large scale equipment where the φ factor of a vessel will be close to unity; that is, the thermal mass of the vessel will be low compared to the thermal mass of the reaction mass and, therefore, can be neglected.

7. Determination of ΔHr

Determination of ΔHr from measurement of Heat Removed by Cooling Medium

7.1. From heat removed by cooling water:

ΔHr can be determined by measuring heat removed by cooling the reaction mass with water passed through cooling coil circuit of vessel and measuring the heat removed from following formula

$$Q_{\text{cal}} = \Delta H_r \times (\text{Reactant mass} / \text{Reactant Mol. Wt}), \text{ cal} = m \times C_{pw} \times \Delta T_w, \quad (\text{vii})$$

Where m is mass in gms of cooling water, Cpw is specific heat of water, 1 cal/gm °C and ΔTw is outlet water temperature (T₂) minus inlet water temperature (T₁).

7.2. By calculating ΔHr from determination of heat removed, Q, from Heat Transfer Coefficient, U, of the system.

As mentioned earlier, U can be determined by simple experiment from formula (v)

$U = Q / (A \times \Delta T_{lm})$ Once 'U' is known for process system, Q and ΔHr can be calculated from equations (va) and (vb).

8. EXPERIMENTAL AND RESULTS

Experiments were carried out at full charge capacity of the autoclave and desired temperatures and heat generated was removed by passing cooling water through coil inside the vessel and measuring heat removed from equations (vii) and (v). Overall Heat Transfer coefficient, U, of the autoclave with process mass used for the experiments was determined from **Exp. 1** below.

8.1. Exp. No. 1

Determination of Heat Transfer Coefficient, U,

Charge: Schiff base: 1170 gm; Solvent : 630 gm.

- Reaction Mass Temperature, T = 60°C, Cooling Water Flow Rate = 84 ml / min, or (84/60) ml / sec.
- Under stirring, the mass was kept at equilibrium for 10 minutes.
- Water Inlet Temperature, T₁, was at 36°C; Water Outlet Temperature, T₂, was at 56°C.
- Cooling coil dia: 0.373/100 m.; Cooling coil length: 4.38 m.
- Cooling coil area, A = 3.143*0.00373*4.38 = 0.05135 m²
- ΔT_{lm} = ((60-36) – (60-56)) / ln ((60-36)/(60-56)) = 25.70 °C
- Heat removed per sec. Q = mass* Temp. difference*Cp = (84/60)* (56-36)*1.0 = 28 cal/sec
- Therefore, from eq. (v), U = 28 / (0.05135*25.7) = 21.22 cal / sec.M²°C

8.2. Exp. No. 2

ΔHr from Heat Removed – Eq. (iv)

Charge: Schiff Base: 1170 gm.; Solvent: 630 gm ; Cooling water rate: 110 ml/ min ; H2 Press: 10Kg/Cm2

Reaction Removed	Reaction	Water Inlet Heat	Water Outlet	Water	Heat Removed
Time	Temp. °C	Temp. °C	Temp. °C	Collected, ml	Calories
23 min	60-65	31	56-59	2530	67045
27 min	55-60	31	52-56	2970	67390
42 min	50-55	31	47-52	4620	85470
75 min	41-50	31	37-47	8250	90750
TOTAL					311655

Table 1 Experimental details

The experimentally determined apparent $\Delta H_r = 311655$ Calories (A)

Theoretical ΔH_r for the Schiff Base is = 29636 Calories / Mole i.e for 236 gms

Therefore, Theoretical ΔH_r for the experiment = $29636 \times 1170 / 236 = 144413$ Calories

Excess apparent $\Delta H_r = 311655 - 144413 = 167242$ Calories likely from cooling of the reaction mass and reaction vessel from 65°C to 41°C.

8.3. Exp. No. 3

Determination of ΔH_r from Heat Removed – Eq. (iv) and (v)

Charge : Schiff Base : 1170 gm.; Solvent : 630 gm. Water Flow Rate : 220 ml / min; H2 Press: 10 Kg/Cm2

To minimize this heat from vessel and reaction mass added to ΔH_r , reaction was carried out at lower temperature of 40°C so as to complete reaction at the same temperature and no heat added or removed from reaction vessel and mass. This lower reaction temperature could be controlled by adjusting hydrogen pressure. The experimental ΔH_r was calculated by

1. From the heat removed by cooling water by measuring mass and average temperature difference of inlet and outlet water and
2. From 'U' value of the system measuring only reaction period.

Reaction	Charge	Water Inlet	Water Outlet	Water collected	Heat Removed
min	Temp.°C	Temp.°C	Temp.°C	ml	Calories
193	40	32.15	36.05	42460	165594

Table No 2. Experimental Details

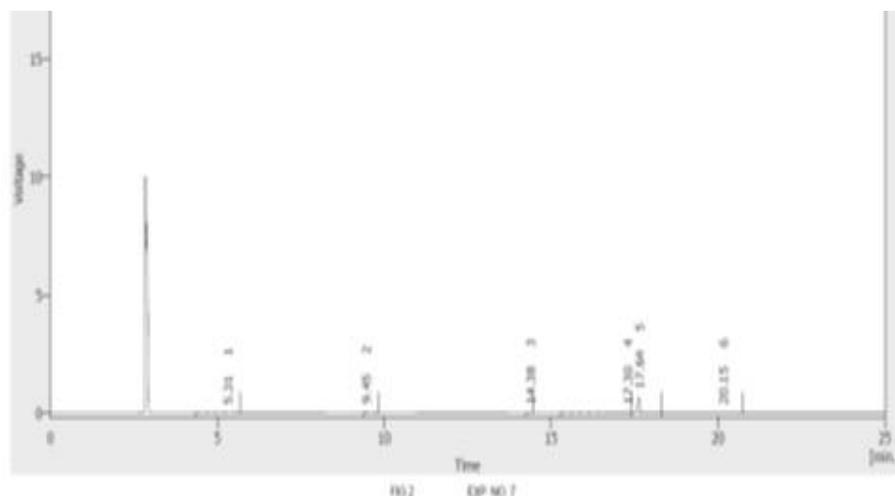
- 'Q' from water measurement and it's temperature difference = **165594 Calories**
- 'Q' from 'U' Value and reaction period

From **Exp. No. 1** , $U = 21.22$ cal/secm²°C ; $A = 0.05135$ m² ;

- $\Delta T_{lm} = ((40-32.15) - (40-36.05))/\ln((40-32.15)/(40-36.05)) = 3.9/\ln 1.988 = 3.9/0.2984 = 13.07^\circ\text{C}$
- Determination of Experimental Heat from 'U' Value of the system :
- 'Q' from 'U' value = $21.22 \times 193 \times 60 \times 0.05135 \times 13.07 = 164918$ Calories

Theoretical ΔH_r for this experiment will be

$29636 \times 1170 / 236 = 146924$ cal. On gas chromatography analysis, Fig. 2, the reaction conversion was found 89.4 %. The theoretical ΔH_r will be = $146924 \times 0.894 = 131350$ cal.



Result Table (Total - MSB - Lab reactor at 40 C, 26.03.2022 on capillary - Detector 2)

	Reten. Time [min]	Area [mV.s]	Area [%]	Compound Name
1	3.313	10.220	0.3	
2	8.450	94.038	3.1	
3	14.380	7.777	0.3	
4	17.300	28.811	0.9	
5	17.640	2742.500	89.4	
6	20.153	9.976	0.3	
7	26.283	72.793	2.4	
8	31.907	92.132	3.0	
9	31.243	10.772	0.4	
	Total	3068.919	100.0	

Figure 2. Gas Chromatography Analysis

The observed experimental ΔH_r from heat gained by water is 165594 cal which is about 26 % more than theoretical and from ‘U’ calculation is 164918 which is about 25.6 % more than theoretical. The difference in lab experiment results and theoretically calculated values, though significant, can be basis for plant scale design when safety design factor for exothermic reactions of 25 % overdesign for cooling capacity may be advisable. To confirm results of experimental and theoretical ΔH_r being in more acceptable range, larger plant scale data was obtained from same reaction carried in 2000 litre autoclave vessel wherein the ϕ should be nearly 1 and, therefore, reactor heat losses can be neglected. As explained above under **Exp. No. 3**, the reaction was carried out at lower temperature so as to complete the reaction at constant temperature. At lower temperature, the heat loss to environment will also be minimum.

8.4. Exp. No. 4

Equipment : 2000 litre SS 316 Pressure Vessel (Autoclave) - Fig. No. 3

Charge : Schiff Base : 935 kgs.; Solvent : 504 Kgs.; H2 Press : 10 Kg/Cm2

Procedure: The reaction was carried out as described in the lab scale experiments at average maintained temperature of 46.6 °C so as to complete the reaction at the same temperature and, therefore, no heat transfer to or from reactor. Temperatures of inlet and outlet water were recorded over the period and average reported.

Reaction	Charge	Water Inlet	Water Outlet	Water	Heat Removed
Period, Min	Temp.°C	Temp.°C	Temp.°C	Collected,Lit	Kilo Calories
300	46.6	29.3511	35.186	18566	108331

Table No 3. Experimental Details



Figure 3 Reactor Set up

Theoretical ΔH_r for this experiment will be $935 \times 29636 / 236 = 117414$ Kilo Calories which is about 8.4 % more than observed in the experiment and is within acceptable range for process design for working out cooling capacity. The reaction mass was analyzed for extent of reaction by gas chromatography, fig. 4, and the desired reaction was found 92.9 % complete and with some unknown side reaction. Difference of 8.4 % in theoretical and experimental ΔH_r may be because of this variation in theoretical and practical reaction.

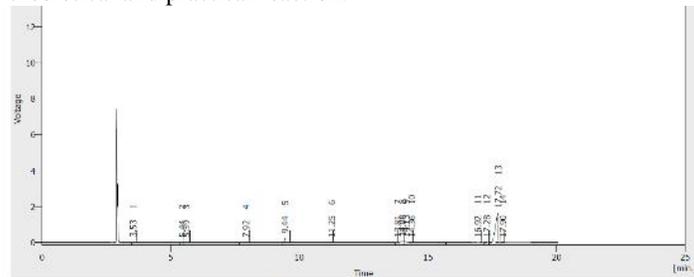


FIG 4 EXP. NO 8

Result Table (Excel - GC4 1 TM 901_04_09_2022 - Detector 2)

Reten. Time [min]	Area [mV.s]	Area [%]	Component Name
1	3.530	40.747	0.4
2	5.427	11.100	0.1
3	5.593	8.196	0.1
4	7.023	2.874	0.1
5	6.437	476.323	3.6
6	11.253	6.792	0.1
7	11.810	3.089	0.0
8	15.067	163.367	0.8
9	14.533	82.936	0.7
10	14.257	8.528	0.1
11	16.023	27.801	0.2
12	17.777	75.865	0.6
13	17.720	11436.782	90.9
14	17.500	15.712	0.1
Total	12366.675	100.0	

Figure 4. Gas Chromatography Analysis

From the data of this same plant scale reaction, product of Heat Transfer Coefficient and cooling area for the plant cooling system was determined as below :

$$\Delta T_{lm} \text{ for the reaction} = ((46.6-29.3511) - (46.6-35.186)) / \ln ((46.6-29.3511) / (46.6-35.186))$$

$$= 5.8349 / 0.1793 = 32.592 \text{ } ^\circ\text{C}$$

$$\text{From equation (v), } U \cdot A = Q / \Delta T_{lm} = 108331 / (300 \times 32.592) = 11.0795 \text{ Kilo Cal/min}^\circ\text{C}$$

This value of $U \cdot A$ was used to determine heat removal, Q , from known ' $U \cdot A$ ' value for next experiment.

8.5. Exp. No. 5

Determination of ΔH_r from U value

The reaction was carried out as per Exp. No. 4 with slight variation in reaction conditions.

- Reaction Period : 380 min. Average reaction mass temp. : 41.20 °C
- Average water temperature : Inlet : 27.49 °C; Outlet : 33.41 °C
- From this data, as per equation ix, $\Delta T_{lm} = 5.92 / \ln (13.71/7.79) = 24.114$ °C
From equation viii,
- U*A value from Exp. No. 8, heat removed, Q, per minute = 11.0795*24.114 = 267.171 cal / min.
- Therefore, total heat removed = 267.171*360 = 101525 kilo calories.

This is about 11.5 % lower than ΔH_r , theoretical as against 8.4 % in **Exp. No. 4**.

9. Results & Observations

Several laboratory experiments were carried out for determination of ΔH_r for catalytic hydrogenation under pressure in pilot autoclave. Since the reaction is carried out under pressure, the reactor used was heavy duty with mass of several kilograms of stainless steel, several times the reaction mass.

The reaction was carried out at full capacity and when stable initial temperature of reaction mass and reactor is reached (**Exp. No.2**), maintaining this temperature by continuously removing ΔH_r by cooling water and measuring this heat. Here, the temperature could not be maintained at constant level and dropped due to decrease in rate of reaction and ΔH_r measured also included heat removed from reaction vessel and reaction mass for cooling. In this case calculated ΔH_r was much more than theoretical ΔH_r .

Exp. No. 3 was carried out at lower temperature of 40°C so as to complete the reaction at constant temperature, maintaining reaction mass and reactor temperature at initial level till end of reaction so that no heat is transferred from or to reactor and reaction mass. ΔH_r measured in this experiment from heat removed by cooling water was 26 % more than theoretical. For the same experiment, ΔH_r was also calculated from 'U' value for the system, as determined by **Exp. No. 1**, and it was found about 25.6 % more than theoretical. The difference in ΔH_r values found by measuring heat removed by cooling water and from 'U' value is almost negligible for design purpose. This excess experimental heat can be due to possible side reactions which are not accounted for in calculation of ΔH_r , theoretical and is near safety design limit (25 %) of cooling capacity.

To verify the lab scale results on plant scaled up process, **Exp. Nos. 4 and 5** were carried out in 2000 litre plant autoclave and experimental ΔH_r determined by actually measuring heat removed by cooling water and from 'U' value were compared with theoretical ΔH_r . The results are summarized below :

ΔH_r , theoretical = 117414 Kilo Calories

ΔH_r , experimental from water measurement = 108331 Kilo Calories

ΔH_r , experimental from 'U' value = 101525 Kilo Calories

This variation in ΔH_r values on plant scale, which at maximum is about 16 %, that can be attributed to lower extent of reaction, by-product formation and experimental deviations, is still well within safety margins of process design. A stark difference between results of **Exp. No. 3** (lab scale) and **Exp. No. 4** (plant scale) is whereas in lab scale ΔH_r experimental is more than ΔH_r theoretical, it is reverse in plant scale experiment. This may be explained as a result of variation in reaction kinetics resulting in difference in extent and by-product formation on plant scale. This is evident from the time to complete reaction which is almost double at plant scale.

10. Calculation of Cooling System Parameters

From **Exp. No 3**, Theoretical Q for the reaction mass of 1800 gm is 146924 cal and Experimental Q is 165594 cal. We will take higher of these values, i.e., 165594 cal as base for design purpose. Adding 25 % safety margin, the cooling system should be able to remove 207000 cal of heat from the reaction mass over entire process for 1800 gm of reaction mass on plant scale.

For the process we will have following assumptions:

- The reaction mass is 1800 kg.
- 'U' value for the system is 350 W/m²°C or 83.165 cal/sec°Cm²
- Reaction temperature is 50°C
- The reaction period is 4 hours or 14400 sec.
- Inlet and outlet cooling water temperatures to be 25°C and 40°C respectively
- Total heat to be removed, Q = 207000 Kilo Calories over 4 hours

ΔT_{lm} for the system = $((50-25) - (50-40)) / \ln ((50-25) / (50-40)) = 15 / \ln 1.5 = 15 / 0.1761 = 85.18^{\circ}\text{C}$

From equation (va), $Q = U \cdot A \cdot \Delta T_{lm}$, or per M^2 area, $Q = 83.165 \cdot 14400 \cdot 85.18 / 1000 = 102010$ Kilo Calories. Therefore for removal of 207000 Kilo Calories of heat from the reaction mass maintaining temperature at 50°C over a period of 4 hours, cooling surface area required will be $207000 / 102010 = 2.029 \text{ m}^2$. On the similar line, if cooling surface area for an existing reactor is only 1.0 m^2 , with all other parameters remaining same, the reaction will have to be carried out over extended period of $4 \cdot 2.029 / 1 = 8.36$ hours.

11. Prevention of Runaway Reaction:

The first step to prevent runaway reaction is estimation of heat removal capacity of existing or being designed cooling system.

Estimation of Heat Removal Capacity

If new reactor is being designed, the cooling surface area can be calculated from equation v, typical 'U' values being known for various cooling systems, for example as given below.

Typical U values

- For agitated jacketed glass lined steel vessel cooling - $200 \text{ W/m}^2\text{K}$
- For agitated jacketed glass lined steel vessel (chilled cooling) - $100 \text{ W/m}^2\text{K}$
- For agitated jacketed carbon and stainless steel vessel cooling - $350 \text{ W/m}^2\text{K}$
- For agitated jacketed carbon and stainless steel vessel (chilled cooling) - $150 \text{ W/m}^2\text{K}$
- For well-designed cooling coil inside the vessel - $400 \text{ to } 600 \text{ W/m}^2\text{K}$

Q in equation (v) will be $\Delta H_r / t$, where 't' is reaction period.

For calculating ΔT_{lm} , cooling water inlet temperature will be ambient and outlet 15 to 20°C higher than inlet water temperature. For the existing reactor and cooling system, however, cooling system may not be adequate to remove the reaction heat efficiently. In such case, following modifications to the process may be considered.

- I. Choose different route of synthesis wherein ΔH_r is within the limits of heat removal capacity.
- II. Carry out reaction using diluent of high C_p to reduce ΔT_{ad} to safe level.
- III. Modify cooling system whereby cold cooling medium such as brine is used or supplementary cooling coil provided.
- IV. Carry out reaction over extended period of time so as to match heat being removed is equal to heat produced per unit of time.

12. Conclusion

From the observations above, it can be concluded that probability of exothermic runaway reaction can be predicted by theoretical estimation of ΔH_r from bond energies or heats of formation of the reactants and products as per reaction equation. This finding can further be supported with simple laboratory experiments within facilities available with MSME units. This method of predicting and preventing a runaway reaction can be easily implemented by MSME units with no requirement of cost preventive calorimetry technique. For newly developed reactor and cooling system, this may be sufficient to prevent the runaway. From heat transfer coefficient, heat removal capacity of the existing reactor can be calculated from simple experiment. It doesn't matter if heat transfer area is not known for existing equipment because product of heat transfer coefficient, U, and area, A, ($U \cdot A$) can also be used for calculation for existing system. Mentioned preventive measures will reduce the demand for protective system measures need to be considered for potential runaway reactions. They are containment within reactor system by designing to withstand maximum pressure, emergency pressure relief using pressure release valves and / or rupture discs, Reaction inhibition by addition of inhibitors / catalyst poisoners, discharge to secondary containment and quenching. Further, the method can be followed in house with no concern of technical information leakage.

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