UPGRADING AN ALKOXYLATION FACILITY: THE VALUE OF CALORIMETRIC STUDIES

Dr. Richard L. Rogers and Dr. Klaus Hermann
INBUREX Consulting GmbH, Hamm, Germany

This paper describes the approach used during the upgrading of an Alkoxylation facility which resulted in the removal of the reactor bursting discs thus avoiding the need to install dump tanks. Inherently safe operating conditions, now ensured by a high integrity process control system, were determined by extensive calorimetric studies to measure the heats of reaction and degree of accumulation during the process. The experimental methods used to characterise the highly exothermic desired and runaway reactions which show non-ideal temperature-pressure behaviour and, in the case of ethylene oxide, are also highly toxic are described. The evaluation of the results obtained and justification for the decisions taken are elaborated in the paper.

Alkoxylation, ethylene oxide, venting, inherent safety, calorimetry

INTRODUCTION

The Alkoxylation facility before the upgrade consisted of 6 reactors (volumes up to 6 m³)with associated feed vessels for Ethylene Oxide and Propylene Oxide and was operated under complete manual control. Reactions were carried out using a semi-batch mode i.e. pre-charging of the various substrates with the subsequent addition of the Ethylene or Propylene Oxide at a rate commensurate with available cooling. The reactors were fitted with a safety valve set to open at 1 bar below their design pressure (this ranged from 8 to 10 barg) and a bursting disc with a set pressure equal to the design pressure. The relief vents from both the safety valves and bursting discs (diameter up to 150 mm) vented direct to the atmosphere above roof level. The Ethylene Oxide and Propylene Oxide feed system was also fitted with a hard-wired trip system which automatically stopped addition above a set temperature and pressure and also prevented reverse flow back into the feed vessels.

The operating procedure used was to pre-charge the substrate and catalyst at ambient temperature, inert the reactor with Nitrogen gas followed by heating to the desired operating temperature. Ethylene or Propylene Oxide was then charged with cooling to keep the reactor at the process temperature.

An additional safety measure had been implemented following a runaway reaction which occurred in the 1980's due to the rapid reaction of accumulated Ethylene Oxide which had been added before the reaction had initiated. The operating procedure was changed so that an initial aliquot of Ethylene or Propylene Oxide was charged and the reaction temperature and pressure observed to determine whether the reaction had initiated. This was shown by an increase in temperature due to the exothermic reaction and a reduction in pressure due to the reaction of Oxide. Following initiation of the reaction, cooling was applied and the main charge of Ethylene or Propylene Oxide was added at a rate to keep the reactor at the process temperature.

The degree of accumulation was unknown but the resulting runaway reaction was sufficient to cause the bursting disc to open and the reactor contents, including unreacted Ethylene Oxide, were released to the environment. Luckily no injuries were sustained and the released Ethylene Oxide was dispersed to below hazardous levels before the site boundary. A second release of Ethylene Oxide occurred when the bursting disc on one of the 6 m³ reactors prematurely failed during production at a pressure of 5 barg (set pressure 9 barg). Again the Ethylene Oxide released was rapidly dispersed and there were no injuries and hazardous concentrations were not detected.

Following a review of the Alkoxylation facility and future production requirements in 1999 the company decided that the plant did not meet the current technical safety standards (absence of dump or quench tanks on the relief lines) and, in its then current single shift operating mode, would not meet future production demands. A decision was therefore made to both upgrade the facility and increase production.

OPTIONS FOR SAFE OPERATION

It was decided to increase production by working with multiple shifts and to upgrade the safety of the plant to current standards by fitting a dump tank on the relief lines. However, although the relief system had functioned satisfactorily once in the past, it was uncertain whether the bursting discs currently fitted were large enough to cope with the worse case runaway which could occur. The initial aliquot of Ethylene or Propylene Oxide which was charged was different for each process and the quantity had been empirically set based on plant experience of the amount required to ensure the reaction would start. In addition no information was available on the degree of accumulation during the course of the reaction. An experimental program was therefore started to obtain the thermal and pressure data required to specify the required vent area and to design the complete emergency relief system.

During the course of this initial investigation it became clear that the mainly manual process control system used was insufficient to limit the worse case scenario such that the existing bursting discs would be large enough to cope with a possible runaway. The cost of modifying the reactors and fitting of a suitably large dump tank system was such that an alternative basis for safe operation was needed.

The initial reaction hazard data obtained allowed a HAZOP of a typical process to be carried out. As a result of this it became clear that it would be possible to use an automated process control system to limit the hazard potential of the processes. In addition, provided sufficient thermo-chemical data was available to characterise the reactions, the fitting of appropriate safety trips would allow the degree of accumulation of Ethylene or Propylene Oxide to be controlled such that any runaway reaction would remain within the design parameters of the reactors. This option would remove the need for the emergency vents and the associated relief stream containment system. In addition, the automated control system would allow the plant to be run with fewer operators allowing a multi-shift system to be implemented without additional personnel. An extensive calorimetric study was therefore undertaken to obtain the required reaction data.

HAZARDS OF ALKOXYLATION REACTIONS

Alkoxylation reactions are highly energetic with typical heats of reaction of ca. −100 kJ/mol and, as in this case, are usually carried out industrially in a semi-batch reactor mode with the controlled addition of either Ethylene or Propylene oxide under pressure. A review of the hazards associated with reactions involving Ethylene Oxide has been published by Gustin [1]. The major reaction hazards arise from the runaway reaction of unreacted, accumulated Ethylene or Propylene Oxide which can lead to rapid temperature and pressure increases. A further hazard arises from the possible initiation of a decomposition reaction of Ethylene Oxide in the gas phase. Gas phase decomposition is usually avoided by inert gas blanketting to ensure that the concentration of Ethylene Oxide in the gas phase does not exceed 50 vol.% to 60 vol.% [2].

Although Ethylene Oxide is highly reactive, alkoxylation reactions are prone to delayed initiation, i.e. the reaction does not start immediately on addition of the Ethylene or Propylene Oxide though once the reaction starts it proceeds rapidly. The initiation delay is dependant on the substrate, catalyst and operating conditions used and can be affected by minor impurities in the substrate.

In order to assess the possible hazards of such reactions and to develop safe operating conditions, it is necessary to determine the possible accumulation that could occur which, in the event of a mal-operation, would result in a runway reaction. The liquid concentration of unreacted EO or PO can theoretically be calculated from the partial pressure, however mixtures of substrates containing EO or PO are known to show highly non-ideal behaviour and the calculated concentrations can have errors of over 100%. Figure 1 shows a comparison of the calculated ideal and real vapour pressures of mixtures of Ethylene Oxide and 1-Hexanol. The activity coefficients needed to calculate the real vapour pressures of the mixtures have been determined using the modified UNIFAC group interaction method [3]. It can be seen that at a typical process pressure of 7 atm and temperature of 125 °C, the calculated mass fraction of EO in the mixture assuming ideal behaviour is 0.17. In comparison the mass fraction of EO calculated assuming real behaviour is 0.34. It is clear that a much lower concentration of EO in the mixture at a particular temperature and pressure will be assumed if ideal mixture behaviour is used for the calculation. The higher concentrations of EO which would actually be present will result in a more violent runaway in the event of a mal-operation.

Non-ideality estimation methods such as UNIFAC rely on correlations derived from measured mixture vapour pressures. Unfortunately there is relatively little data available for EO/PO systems and such methods can only be used with confidence for safety assessments if the results can be checked against experimental data. Vapour pressures of mixtures containing EO or PO are however difficult to measure due to the high reactivity of the oxides even in the absence of catalysts which are usually used in industrial processes. This is shown in Figure 2 which compares the vapour pressure measurements obtained from mini-autoclave experiments of Propylene Oxide and a mixture of a long chain Fatty Acid and Propylene Oxide without catalyst. It can be seen that even at low temperatures a reaction takes place resulting in a reduction of the total pressure. It is therefore not possible to obtain reliable vapour pressure values from simple mixing experiments.

**CALORIMETRIC MEASUREMENT OF THE DEGREE OF ACCUMULATION**
The alkoxylation of various substrates by EO and PO under pressure was therefore studied to determine the degree of accumulation under industrial operating conditions and mal-operations. A Chemisens RM2 isothermal reaction calorimeter was used with piston pumps for the controlled dosing of the EO/PO. The small reactor volume (200 ml) minimised the quantity of highly toxic EO which needed to be used during the experiments.

As is often the case in fine chemical manufacturing a large number of different substrates are used in the alkoxylation facility. In order to minimise the number of experimental tests, 5 representative substrates where chosen on the basis of their chemical structure and reactivity for the detailed study. Thermal stability tests on the substrates and products involved in manufacturing operations had shown that there was no hazard from exothermic decomposition reactions and that they were stable to temperatures well above those used in the processes.

Experiments were carried out with EO and PO at temperatures and pressures used in the process and also at lower temperatures and differing feed rates to simulate the effect of mal-operations. A typical result for the ethoxylation of a short chain alcohol is shown in figure 3. It can be seen that the rate of reaction, shown by the heat flow curve, closely follows the pressure of EO in the reactor which is representative of the concentration of EO in the liquid phase. For the normal process the rate of reaction can be controlled by the rate of addition of Ethylene Oxide and matched to the available cooling. The degree of accumulation of EO can be calculated from the heat released and the amount of EO added at any point in the process and is represented in figure 3 as the percent EO present compared to the total EO charged. The accumulation of EO increases with increasing pressure in the reactor and in this case reaches a steady value of ca. 20% equivalent to ca. 5 wt% EO in the total reaction mixture. Once addition of EO is stopped, the pressure rapidly reduces due to the further reaction of the EO present. The total heat release of the reaction measured was −113 kJ/mol EO which corresponds well to the typical literature values of −100 kJ/mol EO.

Figure 4 shows the isothermal heat flow calorimeter result for the reaction of Propylene Oxide with a long chain Fatty Acid. In this experiment once the reaction had initiated, the rate of addition of PO was adjusted as in the plant process such that the total pressure remained constant. It can be seen that the heat flow trace shows two peaks indicating a multi-step reaction mechanism. Di Serio et al [4] have proposed such a mechanism for the Ethoxylation of Fatty Acids which can be used analogously to explain the behaviour with Propylene Oxide.

The initial reaction of the Fatty Acid with Propylene Oxide can occur by a catalytic or non-catalytic step where M is the catalyst:

$RCOOH + PO \rightarrow RCOO(PO)H$ non-catalytic

$RCOO^-M^+ \rightarrow RCOO(PO)^-M^+$ catalytic
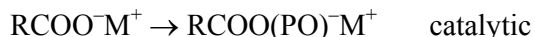
The species $RCOO^-M^+$ is poorly active as a catalyst, therefore the non-catalytic reaction mainly occurs. The catalytic reaction which leads to further alkoxylation only occurs after the complete monopropoxylation of the Fatty Acid substrate. This is confirmed by the heat flow trace observed which shows a minimum after the addition of one mole

equivalent of Propylene Oxide. The further catalytic polypropoxylation reaction, which is slower, then occurs by the catalytic route:

$$RCOO(PO)^-M^+ + PO \rightarrow RCOO(PO)_2^-M^+ \quad \text{propagation}$$

As with the Ethoxylation reactions, the degree of accumulation of PO correlates with the maximum pressure and in this case reaches a maximum of 27% equivalent to 6 wt% PO in the reaction mixture. The pressure drop and further reaction of PO once the addition is stopped is slower than in the case of the Ethoxylation reactions.

In addition to providing the necessary information about the degree of accumulation of EO or PO during the reaction, the isothermal heat flow calorimeter experiments allowed the course of the alkoxylation reactions to be followed during the addition of EO or PO, providing valuable information about the reactivity and solubility of EO and PO in the substrates under the industrial conditions. This data allowed the process operating conditions to be optimised with a resulting improvement in plant utilisation.

CHARACTERISATION OF THE RUNAWAY REACTION

It is clear from the highly exothermic heat of reaction that an unlimited accumulation of EO or PO would lead to a runaway reaction resulting in temperatures and pressures which could burst the reactor. A safety concept based purely on the provision of emergency relief venting is therefore not feasible for such reactions and a high integrity trip system is needed to limit the amount of EO or PO which can be charged. The isothermal heat flow calorimeter experiments which were carried out allowed the specification of the minimum temperature and maximum pressure limits which are required to prevent an unlimited accumulation of EO or PO but which at the same time allow economic operation of the plant.

The measurement of the degree of accumulation during the process and the overall heat of reaction allowed the 'worse credible case' conditions to be identified i.e. the maximum accumulation which would occur when EO or PO was added within the temperature and pressure limits set by the trip system. These conditions were then used in adiabatic runaway reaction experiments as part of the safety assessment for the plant. Tests were carried out using a Phitec adiabatic reaction calorimeter modified to allow rapid addition of EO or PO during the experiment. Initial tests were carried out with the addition of the maximum accumulated amount of EO or PO to the substrate at the process temperature. These showed that although the temperature of the mixture increased as expected, the pressure in the test can decreased due to the reaction of the EO or PO.

Additional tests therefore were carried out with the addition of greater amounts of EO and PO. A typical result for the runaway reaction of Nonyl Phenol with EO in the presence of the catalyst is shown in Figure 5. During the addition of the Ethylene Oxide (17 wt%) over 5 min the temperature initially decreases due to the cooling effect of the added EO. The amount of unreacted EO remaining at the end of the addition was calculated from the temperature and specific heats of the reactants together with the heat of reaction, in this case the unreacted amount of EO was determined to be 13%. Once addition was complete the temperature increased due to the exothermic reaction however, even with this high concentration of EO, the pressure did not increase, it initially remained constant and then decreased.

Further adiabatic tests were carried out to identify possible conditions which could lead to a runaway reaction with increasing pressure. It was found that this would only occur if much higher concentrations of EO were present which could only be simulated by the addition of the EO at a low temperature such that it did not react. Figure 6 shows the adiabatic calorimeter result of the addition 25 wt% EO to Nonyl Phenol. The EO was added at a temperature of 88 °C and the mixture cooled to a temperature of 72 °C at the end of addition. As the rate of reaction was insignificant at this temperature the test cell was heated using a 'Heat – Wait – Search' mode to 81 °C and then 101 °C at both these temperatures negligible reaction occurred. On increasing to the process temperature of 120 °C the runaway reaction started and reached a maximum of 260 °C. The pressure in the test cell at the start of the runaway was 11 bara and increased to a maximum of 14 bara before rapidly decreasing.

The tests confirmed that it is possible to obtain a runaway reaction which results in increasing pressure and reinforced the importance of ensuring that EO or PO is not added at low temperatures at which high amounts can accumulate.

NEW SAFETY CONCEPT
The calorimetric studies confirmed the high energy release of the alkoxylation reactions and showed that once initiated the reactions proceed rapidly. During the normal process the maximum accumulation of EO or PO which occurred within the temperature and pressure limits specified and controlled by a trip system, was less than 7 wt% based on the total reactor contents. Tests on the runaway reaction of mixtures containing accumulated EO or PO showed that in such cases the maximum pressure of the reactors would not be exceeded.

It is clear that the degree of EO or PO accumulation depends markedly on the temperature and pressure and provided these are controlled within set limits 'unsafe' accumulation can be prevented. In addition the maximum fill level of the reactors must be controlled to prevent over-pressure due to thermal expansion of the reaction mixture following the temperature increase due to the runaway reaction.

In addition to the process control system, the reactors were therefore fitted with safety trips to stop addition of PO or EO in the event of mal-operations. A HAZOP study was carried out to identify possible mal-operations and their consequences. As a result the main trips fitted to prevent accumulation and which stop addition were:

1. Low/High reactor temperature
2. Low/High reactor pressure
3. High fill level
4. Low pressure difference between feed oxide vessel and reactor to prevent back flow into feed vessel.
5. Low feed vessel pressure
6. High feed vessel temperature
7. Low cooling water pressure
8. Agitator failure
9. Lower pressure in oil seal stirrer bearing (must be always greater than reactor pressure)
10. High temperature in oil seal bearing

The trip system removed the need for the bursting discs on the reactors and these were removed and replaced with safety valves design to cope with service overpressure and fire scenarios. The relief lines from the safety valves discharged into a water reservoir already existing as part of the safety concept for the Ethylene Oxide storage facility.

CONCLUSIONS

The calorimetric studies carried out to characterise both the desired reactions and credible runaway reactions allowed an alternative safety strategy for the alkoxylation facility to be developed. This was based on a safety trip system. The safety analysis of the new process control system and safety trips showed that there was no need for emergency relief thus avoiding the necessity to install a new containment system to cope with the consequences of a runaway reaction caused by accumulation of EO or PO. In addition the automatic process control system fitted allowed the plant to be operated with fewer personnel. This enabled a multi-shift system to be implemented with the same number of workers thus meeting the increased production requirement.

The study demonstrates the benefit of re-examining the safety concept when an upgrade is carried out and the value of calorimetric data in developing inherently safer operating conditions.

ACKNOWLEDGEMENT

REFERENCES

1. Gustin, J.L., 2000, *Safety of Ethoxylation Reactions*, Hazards XV – The Process, its Safety and the Environment, Symposium Series No. 147 IChemE, Rugby, UK.
2. Britton L. G.: *Use of Propylene Oxide Versus Nitrogen as an Ethylene Oxide Diluent*, Process Safety Progress Vol. 19, No. 4, pp. 199–209.
3. Gmehling, J., Lohmann, J., Jakob, A., Li, J., Joh, R. 1998, Ind. Eng. Chem. Res 37, 4876–4882.
4. Di Serio, M., Di Martino, S., Santacesario, E., 1994, *Kinetics of Fatty Acids Polyethoxylation,* Ind. Eng. Chem. Res. 33, 509–514.
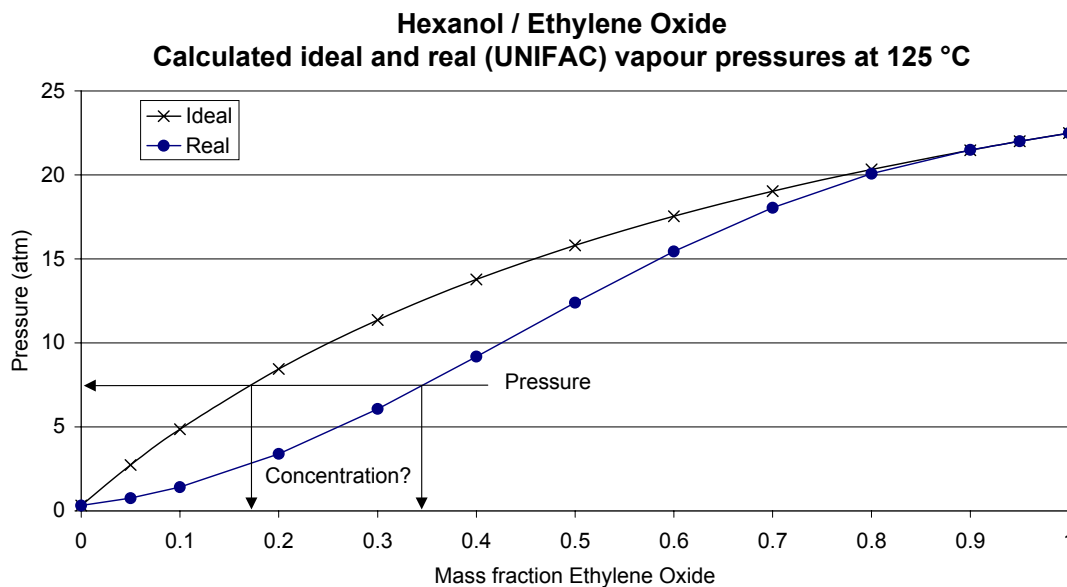
Figure 1.   Comparison of calculated ideal and real vapour pressures of mixtures of hexanol and ethylene oxide
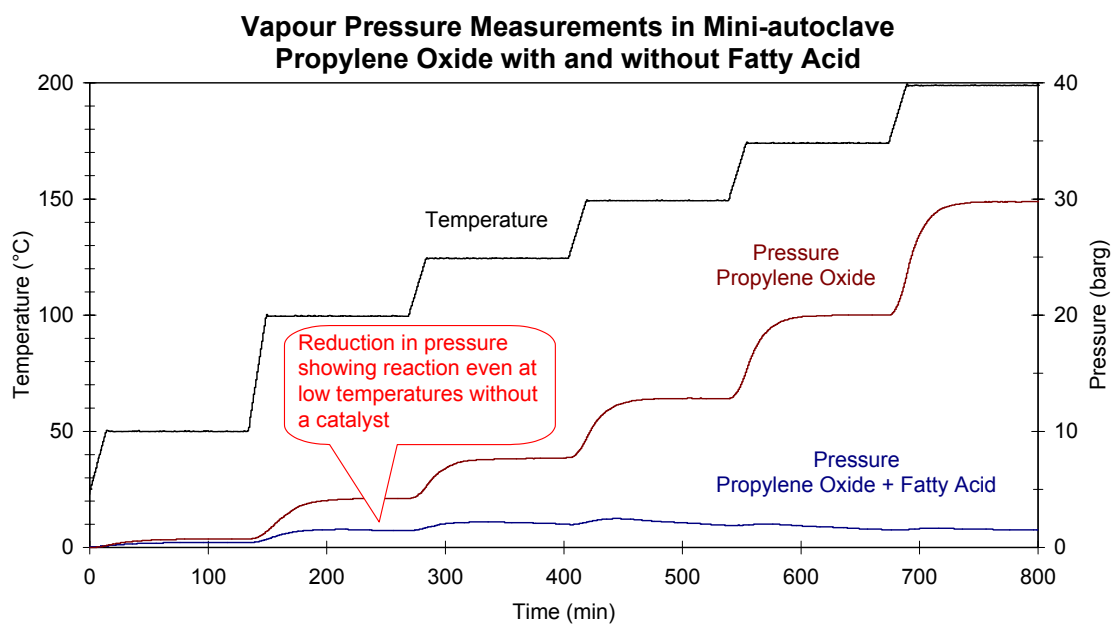

Figure 2.   Comparison of vapour pressures of propylene oxide and a mixture of propylene oxide and fatty acid at different temperatures
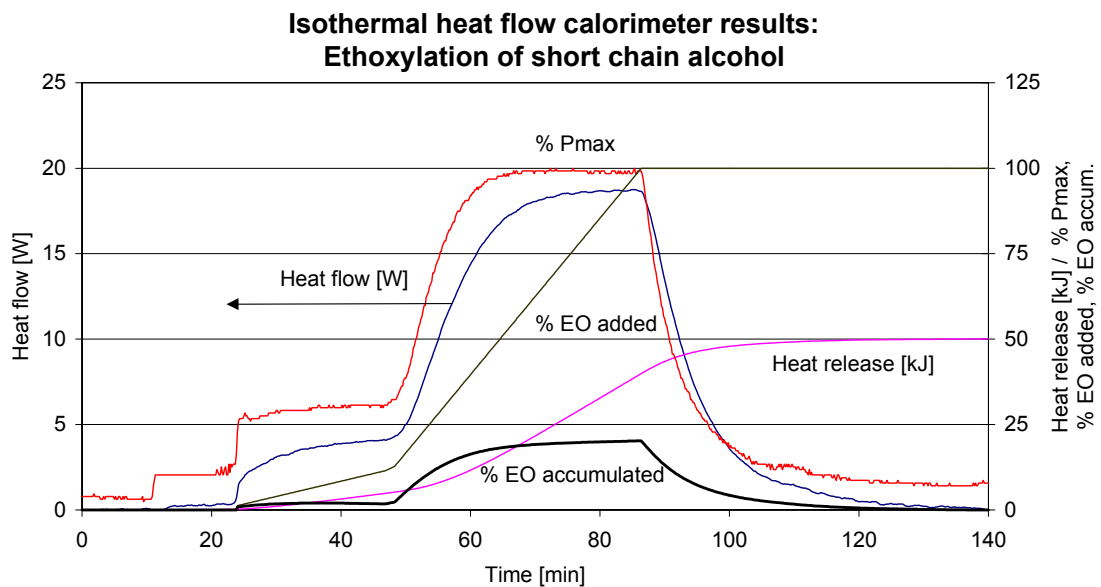
556

**Isothermal heat flow calorimeter results:
Ethoxylation of short chain alcohol**

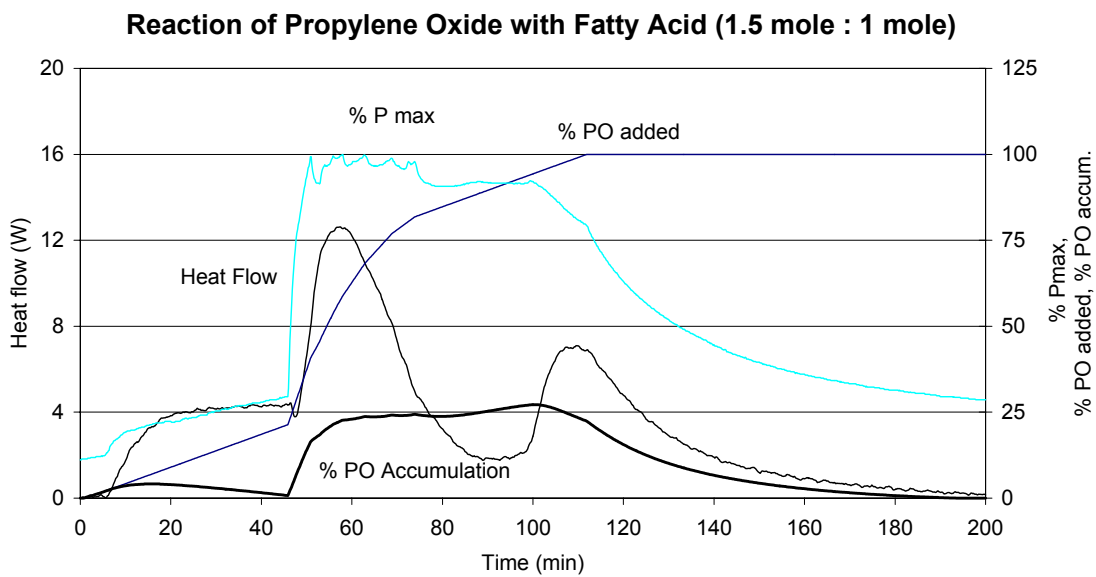**Figure 3.**   Isothermal heat flow calorimeter results of the ethoxylation of short chain alcohol

Reaction of Propylene Oxide with Fatty Acid (1.5 mole : 1 mole)

Figure 4.   Isothermal heat flow calorimeter results of the reaction of propylene oxide with fatty acid

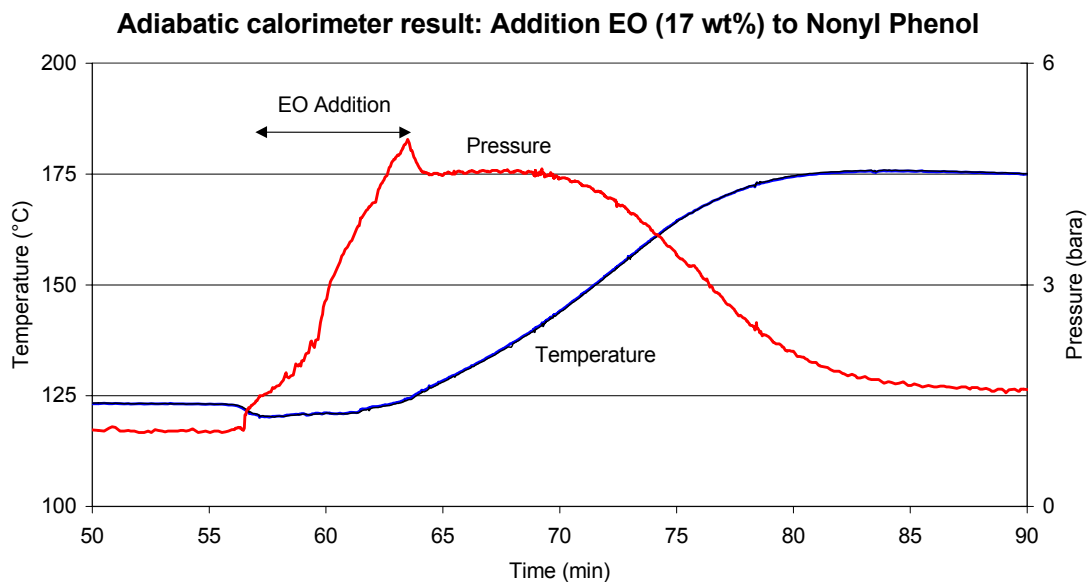**Adiabatic calorimeter result: Addition EO (17 wt%) to Nonyl Phenol**

Figure 5. Adiabatic calorimeter result showing runaway reaction of ethylene oxide (17 wt%) with nonyl phenol

Adiabatic calorimeter result: Addition EO (25 wt%) to Nonyl Phenol
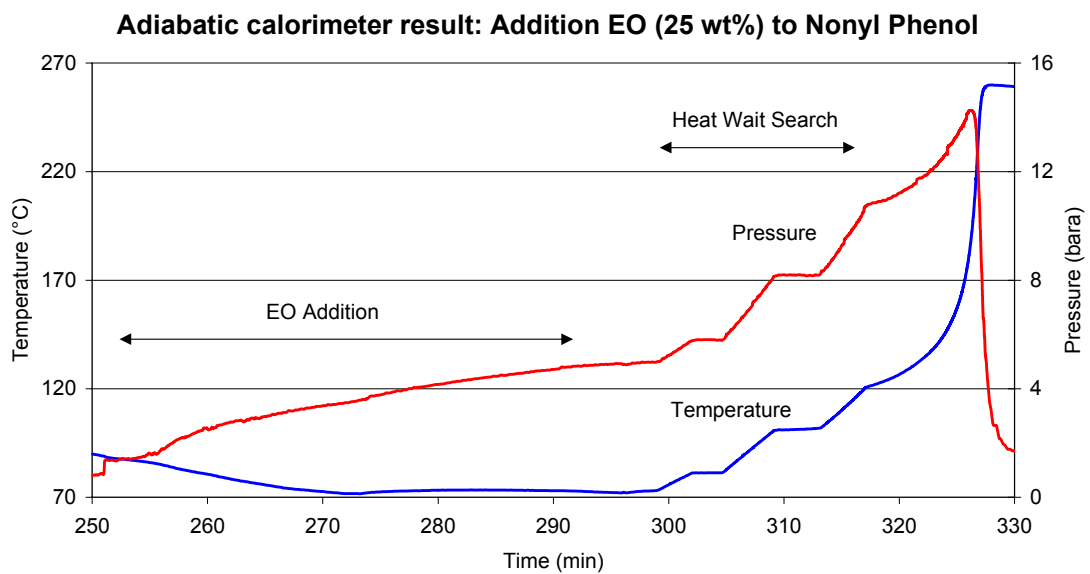

Figure 6. Adiabatic calorimeter result showing runaway reaction of ethylene oxide (25 wt%) with nonyl phenol