

NEW ADIABATIC REACTORS FOR THE
OXYDATION OF METHANOL TO
FORMALDEHYDE

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ABSTRACT OF THE PRESENTATION

Introductory data is given, regarding the activity of CASALE CHEMICALS in the field of methanol derivatives, where formaldehyde is of basic importance, produced world-wide by oxidation of more than 8 million MTPY methanol.

Two fundamental technologies are used for formaldehyde production: those based on a metallic silver catalyst and an excess of methanol, and those using ferric molybdate or metal oxide catalyst and an excess of air. In the recent years consumers have shown a preference for the metal oxide catalyst, generally loaded inside tubes of shell-and-tube type reactors, where a heat transfer media is circulating shell-side. These reactors suffer a certain number of drawbacks, and catalyst life is relatively short.

New adiabatic reactors of CASALE CHEMICALS design offer many advantages in comparison to the tubular, pseudo-isothermal ones, specifically in terms of temperature control, catalyst life, reaction selectivity, direct production of steam.

The presentation describes in detail this new reactor and its performance.

1. INTRODUCTION

CASALE CHEMICALS, the most recently established company of CASALE HOLDING, focuses on processes and products related or complementary to the activities of the sister companies AMMONIA CASALE, METHANOL CASALE and UREA CASALE.

CASALE CHEMICALS is dealing with technologies downstream the methanol production, among which formaldehyde is well known as the chief outlet and a chemistry building block of growing demand.

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Methanol synthesis is a fundamental step for adding value to natural gas. This is because, in turn, methanol is the starting material for the production of a wide range of chemical derivatives.

Fig. 1 is a diagram showing the main industrial products arising from methanol. Let us make a quick survey thereon.

MTBE, methyl terbutyl ether, is an additive for premium grade gasoline, used as an ecological anti-knocking agent, made from methanol and iso-butene. Today MTBE is the second largest volume methanol derivative.

Acetic acid can be obtained from methanol carbonilation. Methyl amines come from methanol and ammonia. Methyl acrylate and dimethyl terephthalate are fundamental molecules for the polymers chemistry.

Now it is also possible to produce olefins from methanol, particularly ethylene and propylene, in a way which is very simple in comparison to any naphtha cracking process.

Dimethyl ether is a further interesting derivative which is growing in interest as ecological replacement of freon in refrigeration equipment and in spray preparations, but also as a clean fuel for the future.

We would like, finally to introduce the most important methanol derivative: formaldehyde, a basic chemical finding its largest volume of application in the manufacture of thermosetting resins. Formaldehyde, in turn, generates a large number of derivatives, as for instance:

- paraformaldehyde, polyformaldehyde: practical ways to handle formaldehyde in concentrate, solid form;

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- trioxane, a reversible trimer as source of anhydrous formaldehyde, and raw material for acetalic resins;
- formic acid, widely used in chemical, pharmaceutical and textile industries;
- urea-formaldehyde concentrate, a pre-polymer for resin production;
- hexamethylenetetramine (called also hexamine or urotropine) a curing agent for thermosetting resins;
- liquid resins, by reaction with urea, melamine, phenol;
- polyols (as pentaerythritol, trimethylolpropane, neopentylglycole) replacing glycerol in the preparation of alkyd resins and coatings;
- injection and compression-molding compounds based on urea/melamine/phenol-formaldehyde resins, reinforced by proper fillers.

Fig. 2 is a table shown quantitatively how the total world output of methanol is shared between its main derivatives. Formaldehyde is the main consumer.

In fact, if all chemicals found in nature or synthesized by man were rated in their order of importance in everyday life, few would outrank formaldehyde. This essential, low cost, industrial building block is utilised for about fifty percent of the total production in the production of thermosetting resins and adhesives. The remainder is consumed in the manufacturing of textiles, papers, paints, wood, furniture, construction, foundry, and speciality chemicals.

The strong importance of formaldehyde has attracted the attention of Casale Chemical S.A., which has investigated possible improvements to the existing technologies, concluding with very interesting proposals for setting up a modernised process based on metal oxide catalyst.

This presentation will deal with a new methanol-to-formaldehyde oxidising reactor of adiabatic type, based on a multi-bed, axial-radial flow path

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configuration. The new reactor is proposed by CASALE either for new plants or for modernisation of existing units.

2. OUTLINE OF THE STATE-OF-ART TECHNOLOGY

2.1 General

Over 90% of the world production of formaldehyde stems from methanol. Two types of processes exist: those using a metallic silver catalyst and an excess of methanol and those using ferric molybdate or metal oxide catalyst and an excess of air.

In general, capital and operating costs for the two processes are not much different, and sometime the choice between them is likely to be determined by the plant location.

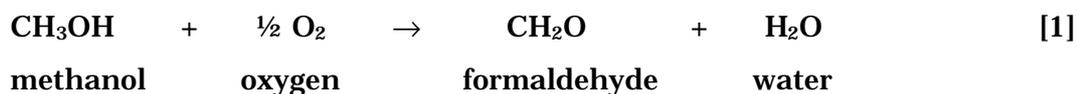
Where some methanol may be left in formaldehyde solutions as a polymerisation inhibitor, the metallic silver catalyst process is probably to be preferred. The lack of demand or outlet for surplus steam also favours this process.

Conversely, the production of solutions with very low methanol content and a good acceptance for surplus steam all work to the advantage of the ferric molybdate process.

In recent years, consumers have shown a preference for solutions low in methanol (less than 1%) and high in formaldehyde (40÷50%) and a majority of new plants have employed a metal oxide catalyst.

2.2 Methanol oxidation with metal oxide catalyst

The overall chemical reaction converting methanol into formaldehyde over ferric molybdate can be simply written as:

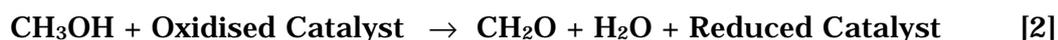


It appears like a partial oxidation of methanol.

Reaction [1] is strongly exothermic and much sensitive to the operating parameters. Its industrial realisation requires the presence of a properly designed catalyst and a careful control of the operating conditions, in order to achieve the necessary stability and to minimise the undesired secondary reactions.

The generally accepted reaction mechanism, related to the vapour phase in presence of iron-molybdenum oxides catalyst involves two consecutive steps:

- methanol oxidation, carried on by the catalyst in "oxidised" status:



- catalyst re-oxidation, carried on by oxygen:



Possible side reactions lead to undesired products, as formic acid or dimethyl ether. Other ones give ultimate oxidation products, such as carbon oxides and water.

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Dealing with metal oxide catalyst, the typical process configuration shown in Fig. 3. Methanol vapours are injected into an oxygen-containing gaseous stream, crossing the catalytic bed of the reactor after preheating.

The heat released by the oxidation reaction is removed from the reactor and is recovered by producing steam.

The gaseous products leaving the reactor are cooled down by preheating the feed gas to the reactor. They are then fed to an absorption column, where formaldehyde is dissolved into water and recovered at the column bottom as final product (called also "formaline").

The gas stream, after formaldehyde separation, is returned back to the gas circulation blower.

Fresh air (source of oxygen) is introduced in the process gas loop, while excess nitrogen (introduced with air) is exhausted to the atmosphere after a proper purification treatment.

A part of the generated steam is used to vaporise methanol; the remaining net difference is exported, or may contribute to drive the gas blower.

2.3 Methanol oxidation in catalytic tubular reactors

Metal oxide catalyst, in form of small cylinders or rings, is loaded inside the tubes of heat-exchanger type reactors, circulating a heat transfer medium on the shell side, to remove the reaction heat. Fig. 4 is a typical state-of-art realisation. In this particular case the heat transfer medium is a molten salt bath, circulated across the tube bundle by an axial pump. Steam is generated inside coils immersed into the molten salt and ending in a separate steam drum. In other cases diphenyl-type fluids are boiled

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tube-side under controlled pressure, and vapours are condensed in a separate waste heat boiler generating steam.

The process gas crosses downwards the catalytic tubes, which are about one meter long.

The operating pressure, process side, is slightly higher than atmospheric.

The heat generated by the exothermic reaction is removed across the catalytic tubes surface. The rate of heat generation and heat removal balance along the tubes, so that a typical temperature profile is reached in steady state conditions, as shown in Fig. 5. In the initial part of the tube the process gas is pre-heated by the hot fluid outside the tubes, then the oxidation reaction starts spontaneously, generating a large amount of heat, which raises the gas temperature up to a maximum, wherefrom it is cooled down by the prevailing heat removal phenomena.

The maximum temperature value depends also on the actual methanol concentration in the feed gas, which is limited in turn by the possible formation of flammable mixtures with oxygen.

The drawbacks of the tubular reactor type are at least the following:

- limited tube diameter, to provide sufficient heat exchange surface per unit of catalyst volume: largest tubes are 1" BWG 16, or 22.1 mm I.D., which is only 4÷5 times the catalyst particle size;
- difficulty to guarantee uniformity of catalyst bulk density inside tubes, as consequence of the low tube/particle size ratio. Non-uniformity reflects on uncontrolled gas flow distribution between tubes, largely affecting local temperature gradients;

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- presence of a localised hot zone where the reaction heat release is maximum, with possible local predominance of undesired side reactions;
- reduced catalyst life, due to deterioration phenomena connected to the relatively high operating temperature, markedly at the hot zone as a consequence of re-adjustment of the atomic structure, reduction of the surface area by degradation of the pore characteristics, volatilisation of molybdenum;
- substantial increase in pressure drop across the catalyst bed, due to above ageing effects, with consequent increase in gas compression power demand;
- difficult catalyst unloading due to sinterisation phenomena;
- use of an intermediate heat transfer medium between the reaction unit and the steam generation unit;
- high reactor cost, requiring thousands of small catalytic tubes to be properly welded to relatively thick tubesheets;
- limited maximum reactor size and production capacity.

3. NEW DESIGN FOR METHANOL OXIDATION REACTORS

The wide experience accumulated by CASALE in the engineering design of fixed-bed, catalytic reactors has been a valuable background for facing the new technological aspects of formaldehyde producing reactors.

The basis for the recent developments is the concept of multi-staged, adiabatic methanol oxidiser, using metal oxide catalyst.

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In principle, the methanol oxidation reaction is carried on stepwise, dividing the total catalyst volume in separate stages. The process gas, of a composition similar to the one of tubular reactors, is put into contact with the first catalytic stage after pre-heating up to a temperature sufficient to allow the oxidation reaction to go on spontaneously (200÷230°C).

The amount of catalyst constituting the stage is such as to limit the extent of the reaction, and consequently the amount of released heat, which raises-up adiabatically the gas flow temperature.

The process gas is then cooled down to a proper temperature, before feeding the next stage, where a second portion of methanol is submitted to oxidation.

This sequence of catalytic steps, which alternate with cooling steps, is the basic idea defining the new process.

The typical sketch of the new 5-staged adiabatic reactor following CASALE design is shown in Fig. 6. The corresponding temperature distribution across the reactor stages is shown in Fig. 7: by comparing it with Fig. 3, the better temperature control is evident.

The catalyst is loaded in baskets, similarly to ammonia synthesis reactors, crossed by the process gas in axial-radial direction.

The catalyst baskets are separated from each other. They are loaded with catalyst and are introduced separately inside the reactor.

The adiabatic rise in temperature of each stage is released to a common tubular heat exchanger which occupies the central part of the reactor. Boiler water is circulated inside this heat exchanger, generating medium pressure steam,

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which is delivered by a separate steam drum. The tube bundle is easily extractable from the reactor top.

The temperature inlet to the next stage is then adjusted to the desired value by addition of a minor hot stream by-passing the corresponding section of the heat exchanger.

The same process is repeated for beds 2, 3 and 4 crossed inwards by the gas flow. The last bed is crossed in outward direction.

It is also of interest the possibility of introducing part of the reactants (methanol, air or oxygen) in intermediate positions, in order to optimise the catalyst performance.

Methanol-to-formaldehyde oxidation process over iron-molybdenum catalyst may be conditioned by its sensitivity to the operating parameters. Temperature and flow control, as well as the physical/chemical/dynamic characteristics of the catalyst play a fundamental role.

While temperature and flow stabilisation are entrusted with the automatic control system, the flow distribution control depends on the geometry of the gas distributors constituting the walls of the catalyst-containing baskets. The resulting flow distribution diagram in the cross section of a catalytic bed is shown in Fig. 8.

Catalyst preparation procedure, size and geometry are such as to minimise the parametric susceptibility and to improve the dynamic properties of the system.

Catalyst loading procedure must guarantee the absence of space heterogeneities and structural non-uniformities. Nevertheless this result can be obtained easily, in comparison to the tubular type reactors.

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After conclusion of the experimentation of the adiabatic technology in small scale, a prototype reactor has been designed, constructed and installed in the frame of an existing formaldehyde producing plant. Fig. 9 is a view of this

prototype during installation. The size of this reactor corresponds to the production of 12'000 MTPY formaline 37% strength.

The performance data collected in the first running period have confirmed the expectations and are very promising for the future developments.

In conclusion, the proposed reactor design demonstrates many merits, overcoming the problems raised by tubular reactors, namely:

- absence of use of molten salts of other heat transfer fluids, the cooling being made directly by generating steam. This not only eliminates operating risks and reduces maintenance problems, but also gives up all the equipment required for the heat transfer media circulation, accumulation, condensation, cooling, control, etc.;
- absence of localised hot zones thanks to the fractionation of the catalyst volume into several portions evenly fed by a careful gas distribution. This increases the reaction selectivity and prolongs the catalyst life, as a consequence of the reduced average temperature, minimising ageing effects. The pressure drop across the catalyst remains substantially stable with time;
- reduced start-up period;
- easy catalyst accessibility, and then reduced replacement time;
- possibility of inter-stage reactants feed;
- lower reactor cost, due to the simpler mechanical design;

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- possibility to realise very large plant capacity based on a single reactor.