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Optimization of the methanol oxidation over iron–molybdate catalysts

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ABSTRACT

The oxidation of methanol on industrial iron–molybdenum catalysts was investigated with a view to shed more light on the possibilities to optimize the process. Stainless steel pseudo-isothermal reactor, located in a precisely controlled thermostat was used to ensure conditions of the process as close as possible to the industrial. The catalytic activity was evaluated under steady state conditions and methanol conversion above 99.0% on the basis of the shape of the temperature profile in height of the catalyst layer, the situation of the “hot spot” and the temperature of the gas flow at exit of the catalyst layer. The outlet gas mixture was analyzed for CH_2O, CH_3OH, CO, dimethylether (DME), and CO_2 content in the analytical section.

The influence of the process parameters on the catalyst activity and selectivity was analyzed and it was concluded that oxygen concentration in the feed mixture has to be equal to or higher than the methanol concentration and water concentration in the range of 2.0–3.0% does favor the selectivity of the process. The increase of methanol concentration in the gas mixture fed in the reactor leads to a dramatic change both of the temperature profile of the catalyst layer and the distribution of the reaction products.

A number of laboratory experiments were performed to clarify the influence of the most important parameters of the process (temperature, space velocity and methanol concentration) on the efficiency of the adiabatic layer.

1. Introduction

It is well known that the iron–molybdate catalysts used in practice have good activity and relatively high selectivity [1,2]. Despite that, several issues still remain open for discussion and in search of new solutions. They are mostly connected with the requirements of current technologies for production of adhesives and plastics that need formaldehyde free of residual methanol (<0.5%), and are also connected with decreasing the quantity of side products and lowering the prime cost of production. In order to meet these requirements it is necessary to search for conditions to implement the process, during which the total level of methanol conversion is over 98.0%, and the selectivity—over 92%. In our research these conditions will be designated as “acceptable”.

The most important results from the investigations of oxide catalysts for selective oxidation of methanol, carried out during the last two decades, lead to the conclusion that the system $Fe_2(MoO_4)_3$–MoO_3 has no alternative [1,3,4]. The problem with the selectivity, however, remains open. The reasons for this are the side reactions which take place and most importantly the secondary formaldehyde oxidation. One solution to this problem is the multi-stage methanol oxidation which leads to a substantial decrease of the temperatures in the catalyst layer. Casale Cemicals SA proposed a new, five-stage adiabatic reactor [5]. The main idea is to limit the degree of conversion of the methanol in each catalytic bed to approximately 20% of the total quantity of methanol fed to the synthesis reactor.

Very often the manufacturers use an additional adiabatic layer or an additional reactor situated under the main one [6,7]. Although this approach is widely popular in practice, there is a complete lack of research in this direction in the scientific literature. This necessitates working by intuition, thus risking serious losses resulting from secondary oxidation of the formaldehyde obtained in the main reactor. A major disadvantage of the adiabatic layer is the impossibility to control the processes that take place inside of it, which may lead to serious economic losses.

With the aim of increasing equipment efficiency the manufacturers often increase the concentration of methanol in the feed gas up to 8.0–10.0% [3]. The results from the industrial experiment described in EP 1 166 864 A_1 [6] show that the increase of the methanol concentration from 7.0 to 8.0% leads to an increase in the content of non-reacted methanol in the reaction gases coming out of the main reactor from 0.25 to 0.56% and to more intensive oxidation processes taking place in the adiabatic layer. The impossibility for heat exchange in the adiabatic layer leads to a significant increase of the temperature, which reaches 300–340 °C, and to a significant increase of the share of side reactions, mainly secondary oxidation of formaldehyde to CO.

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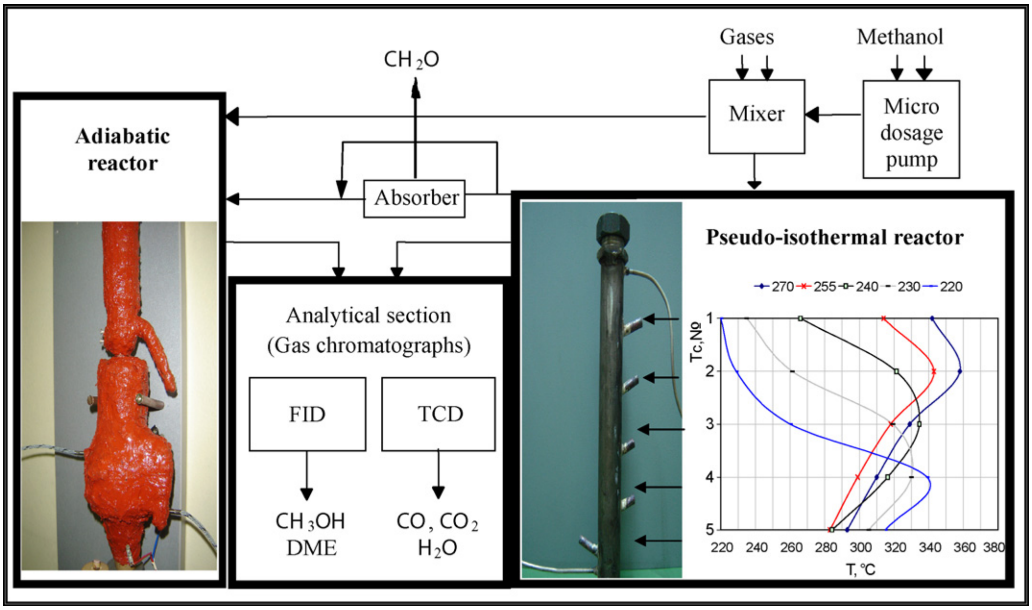

Fig. 1. Schematic diagram of the experimental set-up.

Resolving the problem with the selectivity of oxide catalysts requires deep knowledge of the process mechanism and many papers have been devoted to this problem. Most of them offer a precise and acceptable model of the process [8–10]. The main disadvantage is that investigations are frequently carried out under conditions too different from the industrial ones. Obviously it is also necessary to study the behavior of the catalyst under process conditions which are the closest possible to the industrial, and this is the first purpose of the present study. The second purpose is to shed more light on the possibilities to optimize the process of selective oxidation of methanol over oxide catalysts by using an adiabatic layer.

2. Experimental

All experiments were carried out on a flow apparatus for estimation of oxide catalysts for methanol oxidation using a stainless steel pseudo-isothermal reactor (up to 60 cm^3 catalyst), located in a precisely controlled thermostat as a "main" reactor and a glass adiabatic reactor (up to 20 cm^3 catalyst), also acting as an adiabatic layer (Fig. 1).

The necessary gases (nitrogen and air), after a passage through a drier for moisture elimination, are led in the mixer. They are dosed through special valves with precision ±1.0 l/h. Liquid methanol and water are injected into the gas flow with a micro-dosage pump with capacity 10–100 g/h and precision ±0.3 g/h, included in the experiment interval. The temperature of the heat transfer fluid (air) is maintained with precision ±0.5 °C. Industrial catalyst produced by NEOCHIM SA according to BG Patent No. 60779 B_1 [11] was used. The main characteristics of the catalyst are presented in Table 1.

The content of the gas mixture entering the main reactor, space velocity, and temperature regime allows the experiment to be carried out at conditions closest to the industrial ones. The degree of methanol conversion in the first reactor varies from 78.0 to 99.0%, and the concentration of the non-reacted methanol at its outlet—from 0.1 to 1.5%.

Table 1
The main characteristics of the industrial catalyst, used in all experiments.

Chemical composition	81.5% MoO_3–18.5% Fe_2O_3
Shape	Rings: $h = 5$ mm, $R_{in} = 3$ mm, $R_{out} = 5$ mm
BET surface area (m^2/g)	8.0
Porosity (%)	55.3
Bulk density (t/m^3)	0.78

The outlet gas mixture was analyzed by GC using TCD and FID detectors for CO, CO_2, oxygen, methanol and dimethylether (DME) content in the analytical section. The formaldehyde content in the reaction products was determined by the bisulfite method.

3. Results and discussion

3.1. Oxidation of methanol in the main reactor

It is well known that the most wide-spread reactors for methanol to formaldehyde oxidation are formed by about 10,000 catalytic tubes having 18–25 mm inner diameter and 1000 mm high catalytic bed. The tubes filled with catalyst are crossed by the gaseous reactants and externally are lapped by a fluid intended for continuous heat removal, which is not sufficient for an effective reaction in isothermal conditions to take place. This type of reactors ensures maintaining of relatively narrow temperature range along the catalyst bed and is known as "pseudo-isothermal" [6]. Methanol concentration in the feed mixture does not exceed 6–10% by volume depending on the oxygen concentration, which can vary between 5 and 21% by volume, in order to avoid the possible formation of explosive or inflammable mixtures with the oxygen. The temperature of the "hot spot", formed under these conditions, is usually between 330 and 360 °C.

In order to ensure process conditions which are the closest possible to the industrial we used a stainless steel pseudo-isothermal reactor, located in a precisely controlled thermostat. Catalytic activity was evaluated at steady state conditions and methanol conversion above 99.0% on the basis of the shape of the temperature profile in height of the catalyst layer, the situation of the "hot spot" and the temperature of the gas flow at exit of the catalyst layer. The selectivity (S) was calculated in percent as the ratio between the degree of methanol conversion to formaldehyde and the total degree of methanol conversion. $S = X_f/X_t| \times 100$, where X_f is methanol conversion to formaldehyde and X_t is total methanol conversion.

The experiments were performed under the following scheme: (i)"burning" of the catalyst—includes slow temperature increase of

Table 2
Conversion of methanol, product distribution and selectivity versus methanol concentration. Feed mixture: 10.0% O_2, 3.0% H_2O, N_2 to 100%, space velocity 6400 h^{-1}, temperature of the heat transfer media 250 °C.

CH_3OH (%)	Conversion to (%)			X_t (%)	S (%)
	$CH_2O \pm 0.5\%$	$CO \pm 0.3\%$	$DME \pm 0.2\%$		
5.0	91.3	5.3	2.9	>99.5	91.8
6.0	90.9	6.2	2.4	>99.5	91.4
7.0	90.2	7.0	2.3	>99.5	90.7
8.0	84.5	13.2	1.4	>99.5	85.3

the heat transfer fluid, starting from a level where reaction is close to taking off spontaneously at space velocity and methanol concentration lower than the final ones. After a “hot spot” formation, space velocity and methanol concentration increase slowly until reaching the desired value. (ii) Stabilization of the catalyst—includes maintaining of the process parameters constant until reaching constant values for the degree of methanol conversion and selectivity during 2 h.

The most important parameters of the process (methanol concentration, space velocity, oxygen concentration and water concentration) were investigated.

3.1.1. *Influence of the methanol concentration*

In spite of some differences all authors agree that the increase of methanol concentration in the reactor feed enhances the rate of oxidation. Our results are presented in Table 2 and Fig. 2.

The increase of methanol concentration in the reactor feed from 5.0 to 8.0% leads to a dramatic change both in the temperature profile and in the products distribution. The temperature in the higher part of the reactor, however, as well as that in the “hot spot” increases by more than 70 °C. This leads to a considerable increase of the part of consecutive formaldehyde oxidation and to a decrease in the selectivity to unacceptable for the practice levels. The quantity of DME decreases by more than twice due to increase in its oxidation, mainly to formaldehyde. This, however, cannot compensate the considerable decrease of the process selectivity. Our results are in agreement with these of Popov et al. [12] who observed that the increase in the methanol concentration of the reactor feed from 6.5 to 13.0% results in a decrease of the formaldehyde selectivity between 6 and 8%. The advantage from the increase of methanol concentration in the reactor feed is obvious, nevertheless this approach aiming to increase the productivity has to include ensuring of a very effective heat transfer in order to limit the temperature rise to a level of 350 °C.

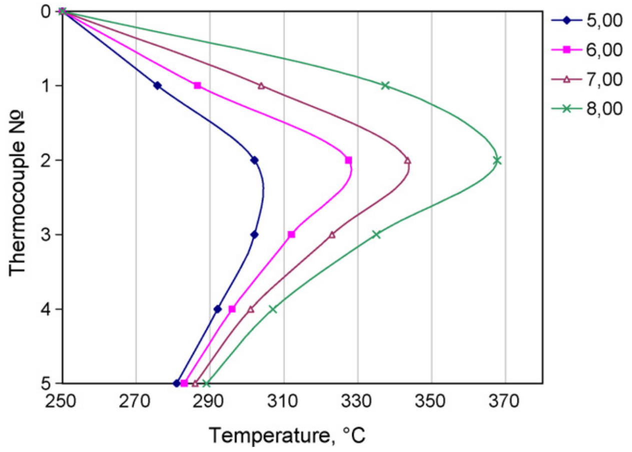

Fig. 2. Temperature profile of the catalyst versus methanol concentration. Feed mixture: 10.0% O_2, 3.0% H_2O, N_2 to 100%, space velocity 6400 h^{-1}, temperature of the heat transfer media 250 °C.

Table 3
Conversion of methanol, product distribution and selectivity versus space velocity. Feed mixture: 6.0% CH_3OH, 10.0% O_2, 3.0% H_2O, N_2 to 100%, temperature of heat transfer media 250 °C.

W (h^{-1})	Conversion to (%)			X_t (%)	S (%)
	$CH_2O \pm 0.5\%$	$CO \pm 0.3\%$	$DME \pm 0.2\%$		
4800	88.6	6.4	4.5	>99.5	89.0
6000	89.8	6.5	3.2	>99.5	90.2
6800	90.0	6.7	2.8	>99.5	90.5
7200	89.8	7.0	2.7	>99.5	90.4

3.1.2. *Influence of the space velocity*

Another means for increasing the installation’s productivity is raising the space velocity of the gas flow. It is known that the space velocity of industrial installations is more often in the range of 5000–8000 h^{-1} and slightly decreases with time. Our results for the influence of space velocity on the temperature profile and products distribution are presented in Table 3 and Fig. 3.

As it can be seen from Fig. 3 the increase in space velocity leads to substantial decrease of the temperature in the upper part and increase in the lower part of the catalyst’s bed. The temperature raise in the “hot spot” is around 25 °C and does not ensue in considerable diminishing of the process selectivity (Table 3). Methanol conversion to CO is nearly the same, while conversion to DME changes substantially. Oxidation of the DME (mainly to formaldehyde) fully compensates the CO increase. It seems that variation of space velocity is a more promising way for improving capacity than substantial increase of concentration, but this approach is limited by the pressure drop along the catalyst’s bed. Taking into account the improved selectivity and the increase in the pressure drop with time, we can conclude that space velocity has to be as high as possible at the start and methanol concentration has to increase slightly in time.

3.1.3. *Influence of the oxygen concentration*

The majority of the authors accepted Mars-van Krevelen’s mechanism for methanol oxidation [13] where only oxygen from the catalyst’s surface is involved in the reaction. The role of gaseous oxygen is to re-oxidize the catalyst. Bibin and Popov [14] found that the rate of methanol oxidation is independent from the oxygen partial pressure. Machiels [15] concluded that for reaction temperatures between 200 and 400 °C the oxygen order in the rate equation is

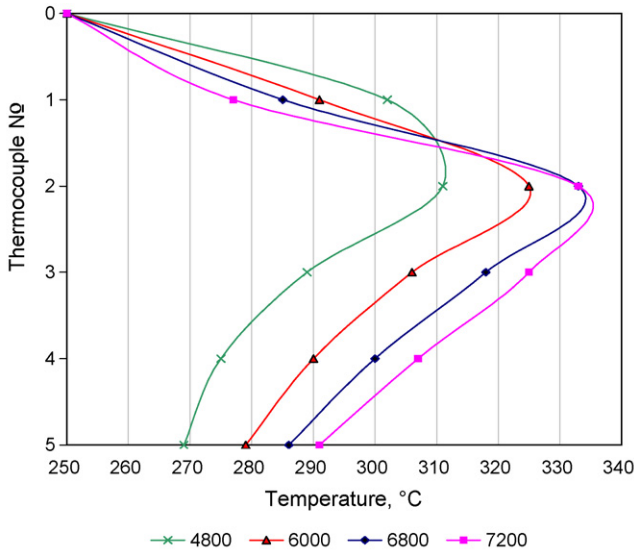

Fig. 3. Temperature profile of the catalyst versus space velocity. Feed mixture: 6.0% CH_3OH, 10.0% O_2, 3.0% H_2O, N_2 to 100%, temperature of heat transfer media 250 °C.

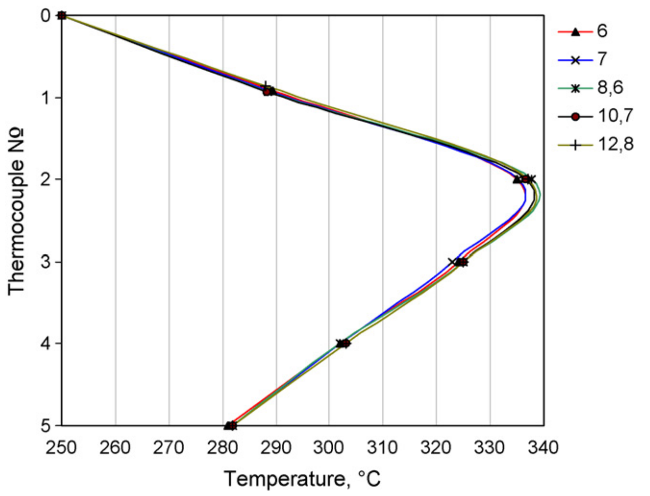

Fig. 4. Temperature profile of the catalyst versus oxygen concentration. Feed mixture: 7.0% CH_3OH, 3.0% H_2O, N_2 to 100%, space velocity 6400 h^{-1}, temperature of the heat transfer media 250 °C.

zero. According to our results (Table 4 and Fig. 4) the same can be concluded for the oxidation of methanol in industrial reactors.

The change in temperature profile is insignificant when oxygen concentration rises from 7.0 to 12.8%. Insignificant is also the change in product distribution and in selectivity. A noticeable change is registered only at oxygen concentration lower than that of methanol. It consists in lowering of the temperature in the upper part of the catalyst layer, and in increase of the methanol conversion to DME. The latter is probably due to the lower degree of methanol to formaldehyde and CO_x oxidation, which in turn exerts a negative influence on the selectivity of the process. The results obtained lead to the conclusion that oxygen concentration in the feed mixture has to be equal to or higher than the methanol concentration.

3.1.4. Influence of the water concentration

The influence of the reaction products on the rate of methanol oxidation has been the object of many investigations. Often the results are extremely different. Jiru et al. [16] concluded that the formaldehyde is responsible for a slight reaction inhibition whereas the water is almost inert. Pernicone et al. [17,18] defend the opposite opinion. According to these authors the formaldehyde has no effect on the methanol oxidation while the water presents a marked inhibition effect. The reason is that methanol and water adsorb competitively on the same active site. Santacesaria et al. [19] also reject Jiru's model and accept that the inhibition effect of water becomes important for high conversion degree. Our results are in accordance with this understanding. As it can be seen from Fig. 5 the temperature profile of the catalyst strongly depends on the water concentration. The absence of water in the feed mixture leads to a very high rate of methanol oxidation and high temperature in the upper part of the catalyst's bed. The successive oxidation of the formaldehyde is considerable and the conversion to CO exceeds 13%. At the same time DME concentration in the outlet mixture is low due to its considerable oxidation under these conditions (Table 5).

The presence of 3% water in the reactor feed increases vastly formaldehyde selectivity. Increase in water concentration in the reactor feed to 6.0% alters the temperature profile of the catalyst, as the temperature in the upper part of the catalyst's bed decreases sharply. The quantity of DME and the selectivity increase rapidly at the expense of the methanol oxidation to CO. It can be concluded that water is a necessary component of the feed mixture. Obviously it can improve the selectivity, but we have to take into account that water is one of the main reaction products and its concentration rapidly increases along the catalyst's bed. This fact limits the water concentration in the feed gas to 2.5–3.5%.

Table 4
Conversion of methanol, product distribution and selectivity versus oxygen concentration. Feed mixture: 7.0% CH_3OH, 3.0% H_2O, N_2 to 100%, space velocity 6400 h^{-1}, temperature of the heat transfer media 250 °C.

C_{O2} (%)	Conversion to (%)			X_t (%)	S (%)
	$CH_2O \pm 0.5\%$	$CO \pm 0.3\%$	$DME \pm 0.2\%$		
6.0	89.5	6.5	3.5	>99.5	89.9
7.0	89.7	6.8	3.0	>99.5	90.1
8.6	90.1	6.9	2.5	>99.5	90.6
10.7	90.0	7.0	2.5	>99.5	90.5
12.8	90.0	6.9	2.6	>99.5	90.5

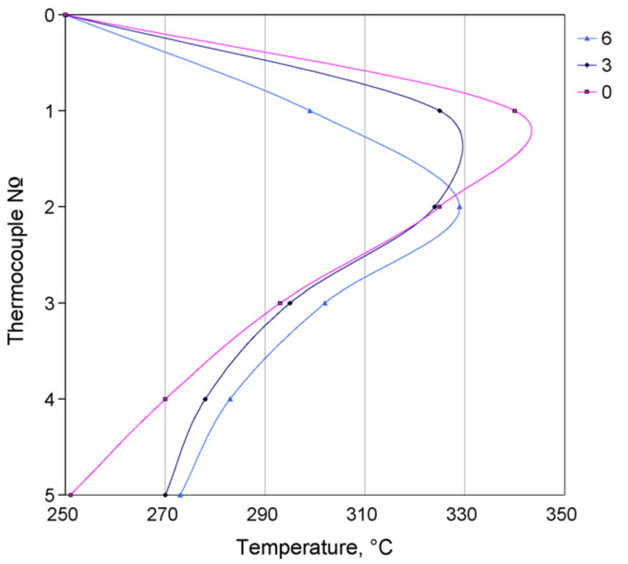

Fig. 5. Temperature profile of the catalyst versus water concentration. Feed mixture: 7.0% CH_3OH, 10.0% O_2, N_2 to 100%, space velocity 4800 h^{-1}, temperature of the heat transfer media 250 °C.

3.2. Oxidation processes in the adiabatic layer

Laboratory experiments were performed to clarify the influence of the most important parameters of the process (temperature, space velocity and methanol concentration) on the efficiency of the adiabatic layer. Feed gas composition of the first (main) reactor through the experiments was constant: CH_3OH—7.0 ± 0.1%, O_2—10.0 ± 0.2%, H_2O—3.0 ± 0.1%, N_2—to 100%. The methanol concentration in the gas entering the second (adiabatic) reactor varied from 0.1 to 1.5%, space velocity—from 8000 to 28,000 h^{-1} and temperature from 210 to 330 °C. The method for determining the borders of applicability of the adiabatic layer will be described in detail only for space velocity 8000 h^{-1}, and only generalized results will be given for the other volume velocities.

Table 5
Conversion of methanol, product distribution and selectivity versus water concentration. Feed mixture: 7.0% CH_3OH, 10.0% O_2, N_2 to 100%, space velocity 4800 h^{-1}, temperature of the heat transfer media 250 °C.

C_{H2O} (%)	Conversion to (%)			X_t (%)	S (%)%
	$CH_2O \pm 0.5\%$	$CO \pm 0.3\%$	$DME \pm 0.2\%$		
0.0	84.5	13.3	1.7	>99.5	84.9
3.0	89.3	8.0	2.2	>99.5	89.7
6.0	89.3	6.1	4.1	>99.5	89.7

Table 6

Total methanol conversion (X_t, %), selectivity (S, %) and product distribution versus temperature. Inlet gas composition: CH_3OH—0.1 ± 0.02%, CH_2O—6.5 ± 0.1%, H_2O—9.7 ± 0.2, O_2—6.6 ± 0.1%, N_2—up to 100%.

T (°C)		Methanol conversion to (%)			C_{MeOH} (%)	X_t (%)	S (%)
Inlet	Outlet	CO	DME	CH_2O			
210	214	3.0	2.0	93.8	0.10	98.6	95.1
220	230	3.6	2.1	93.0	0.09	98.7	94.2
230	241	4.2	2.1	93.0	0.05	99.3	93.6
240	248	4.3	2.0	93.2	0.03	99.5	93.7
250	260	4.4	2.0	93.3	0.02	99.7	93.6
260	274	4.9	1.8	93.1	0.02	99.7	93.4
270	284	5.2	1.6	93.0	0.02	99.7	93.2
280	296	5.5	1.6	92.6	0.02	99.7	92.9
290	306	5.8	1.5	92.5	0.01	99.8	92.7
300	316	5.9	1.5	92.3	<0.01	>99.8	92.5
310	326	6.1	1.5	92.3	<0.01	>99.9	92.4
320	336	6.4	1.5	92.1	<0.01	>99.9	92.1
330	346	6.7	1.5	91.8	<0.01	>99.9	91.8

Table 7

Total methanol conversion (X_t, %), selectivity (S, %) and product distribution versus temperature. Inlet gas composition: CH_3OH—0.3 ± 0.05%, CH_2O—6.3 ± 0.1%, H_2O—9.5 ± 0.2%, O_2—6.8 ± 0.1%, N_2—up to 100%.

T (°C)		Methanol conversion to (%)			C_{MeOH} (%)	X_t (%)	S (%)
Inlet	Outlet	CO	DME	CH_2O			
210	217	2.6	2.0	92.1	0.23	96.7	95.2
220	234	2.9	2.0	92.0	0.22	96.9	94.9
230	244	3.3	2.1	91.7	0.20	97.1	94.4
240	259	3.7	2.2	91.8	0.16	97.7	94.5
250	268	4.1	1.8	92.1	0.14	98.0	93.9
260	277	4.3	1.8	92.3	0.11	98.4	93.8
270	289	4.6	1.7	92.5	0.08	98.8	93.6
280	298	4.9	1.6	92.9	0.04	99.4	93.5
290	311	5.2	1.6	92.9	0.02	99.7	93.2
300	325	5.6	1.5	92.6	0.02	99.7	92.8
310	324	6.2	1.4	92,2	0.01	99.8	92.3
320	348	7.6	1.4	90.8	0.01	99.8	90.8

3.2.1. *Space velocity of the gas flow entering the adiabatic reactor 8000 h^{-1}*

Table 6 presents the dependence of the total methanol conversion (X, %), selectivity (S, %) and product distribution after crossing the adiabatic catalytic bed on the temperature of the gas mixture entering the adiabatic layer at methanol concentration of 0.1%.

In this case the methanol oxidation takes place almost completely in the first reactor and its content in the gas mixture entering the adiabatic reactor is insignificant. It can be seen that the processes in the adiabatic layer take place even at a temperature less than 220 °C. The secondary oxidation of the formaldehyde starts at a temperature of about 220 °C and gradually increases, while its content in the outlet gas after the adiabatic reactor decreases from 93.8 to 91.8% at 330 °C. The quantity of DME remains within the range of 2.0–2.1% up to the temperature of 250 °C at the inlet of the adiabatic reactor, after which it starts to gradually decrease due to its secondary oxidation, mainly to formaldehyde. Obviously the increase of CO concentration in the waste products results from the secondary oxidation of formaldehyde, which increases with the temperature increase and leads to a decrease in selectivity under 92% at 330 °C.

Fig. 6 represents the dependence of the degree of methanol conversion and the selectivity of the process on the inlet temperature in the adiabatic reactor.

The change of both indicators follows clearly defined tendencies. The total degree of methanol conversion increases with the increase of temperature and reaches almost 100% at 300 °C. The tendency in the change of selectivity is contrary—it decreases significantly in the studied temperature interval, reaching 92.1% at 320 °C. Obviously the reasons for that are the processes of secondary oxidation of formaldehyde and DME. The two processes lead to contrary results regarding the selectivity. The oxidation of DME leads to an increase in the production of formaldehyde and the selectivity of the process. This positive effect, however, is completely consumed by the dominating secondary oxidation of formaldehyde to CO, which ultimately leads to a decrease in selectivity. The shaded part of the diagram shows the limits within which the use of an adiabatic layer leads to obtaining “acceptable” results ($X_t > 98\%$ and $S > 92\%$).

The results presented in Table 6 and Fig. 6 make it possible to assess the efficiency of the adiabatic layer and its role in the total process of methanol oxidation at a methanol content in the gas feed of 0.1%. It is obvious that using an adiabatic layer is necessary only in case the methanol content in the produced formalin must be under 0.5 wt%.

Table 7 and Fig. 7 present the dependence of the total methanol conversion, selectivity and product distribution after crossing the adiabatic catalytic bed on the temperature of the gas mixture entering the adiabatic layer at methanol concentration 0.3%.

At such a work regime in the main reactor the formalin produced has a methanol content of about 1.9% and it is most often necessary to use an adiabatic layer. The tendencies already described are valid

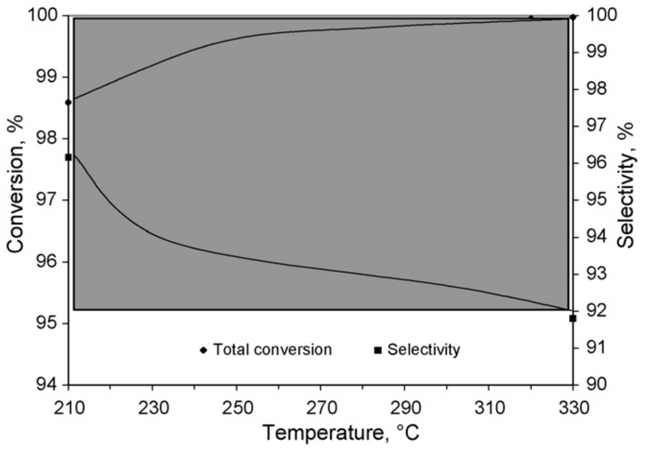

Fig. 6. Total methanol conversion (X_t, %) and selectivity (S, %) versus inlet temperature in the adiabatic reactor. Inlet gas composition: CH_3OH—0.1 ± 0.02%, CH_2O—6.5 ± 0.1%, H_2O—9.7 ± 0.2, O_2—6.6 ± 0.1%, N_2—up to 100%.

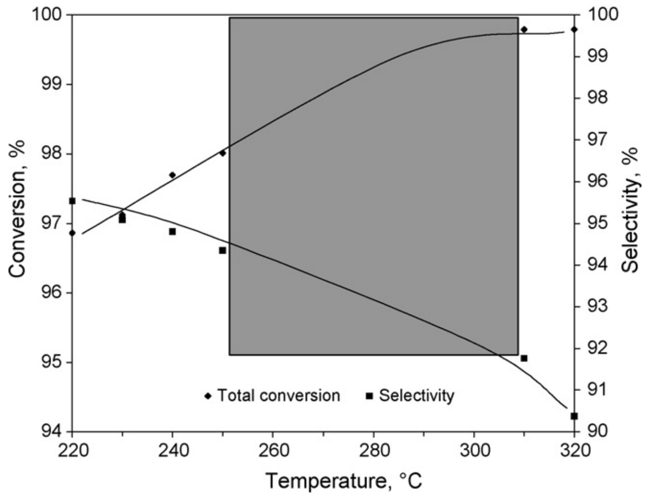

Fig. 7. Total methanol conversion (X_t, %) and selectivity (S, %) versus inlet temperature in the adiabatic reactor. Inlet gas composition: CH_3OH—1.5 ± 0.1%, CH_2O—5.2 ± 0.1%, H_2O—8.2 ± 0.2%, O_2—7.3 ± 0.1%, N_2—up to 100%.

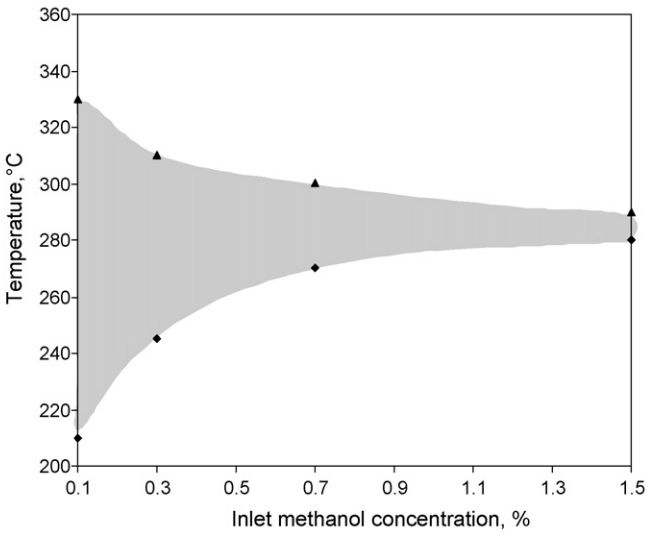

Fig. 8. Borders of applicability of the adiabatic layer at a space velocity of the inlet gas mixture of 8000 h^{-1}.

in this case too. While at a methanol concentration in the gas mixture of about 0.1% the adiabatic layer is applicable in the whole temperature interval from 210 to 330 °C, at a methanol concentration of 0.3% this range is limited from 250 to 310 °C. At a methanol concentration in the outlet gases of the main reactor 0.7 and 1.5% the methanol content in the formalin produced is 4.7 and 11.7%, respectively. In these cases the use of an adiabatic layer is imperative. However, the possibilities to effectively use it are significantly lower. The results obtained reveal that at a methanol content in the gas entering the adiabatic layer of 0.7% they are limited within the temperature interval of 270–300 °C, and at 1.5%—up to 290 ± 5 °C.

The summarized results of the operation of the adiabatic layer at a space velocity of 8000 h^{-1}, presented in Fig. 8, delineate the borders of its applicability as a function of the temperature at the layer inlet and the methanol concentration adiabatic layer.

The figure presents a clearly defined tendency of limiting the temperature interval, within which the adiabatic layer can be successfully used, with the increase of concentration. The limitation is both at the low and the high temperatures. Obviously, the reason for shifting the lower border toward the higher temperatures is the necessity for a higher temperature for complete oxidation of the inlet methanol, especially when its concentration exceeds 0.3%. In the high temperature area there is a significant increase in the role of the processes of secondary oxidation leading to a decrease in the total process selectivity. This renders the methanol concentration in the inlet gas mixture a limiting factor when determining the upper border of applicability of the adiabatic layer.

3.2.2. Space velocity of the gas feed entering the adiabatic reactor: 14,000 and 28,000 h^{-1}

The results for the dependence of the total methanol conversion (*X*, %) and selectivity (*S*, %) on the temperature and methanol concentration of the feed gas mixture entering the adiabatic layer at a space velocity of 14,000 and 28,000 h^{-1}, are summarized in Fig. 9.

In this case, too, the border of applicability of the adiabatic layer is both at the low and the high temperatures.

The practical implementation of final oxidation of the methanol–air mixture in adiabatic conditions at a space velocity of the feed gas under 14,000 h^{-1} is difficult because of economic reasons, and above all the necessity for a significant quantity of a catalyst as well as technical problems with placing it under the main reactor. The obtained results, however, give beneficial information for the possibilities of using an "auxiliary" reactor situated under the main one, which allows relieving the main reactor and boosting installation capacity. Many variants of such reactors are described in EP Patent No. 1 166 864 A_1 [6].

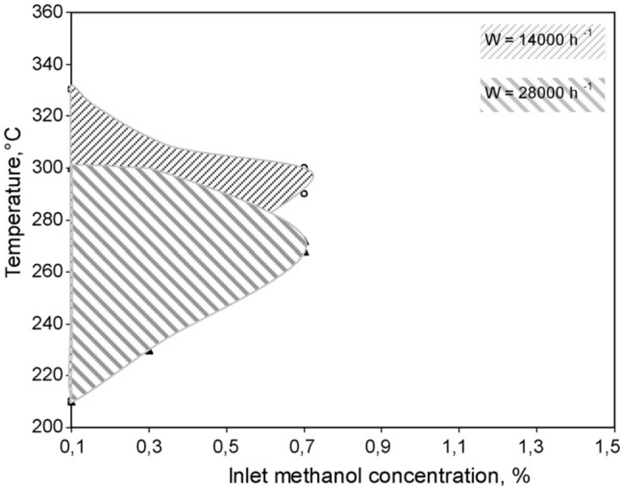

Fig. 9. Borders of applicability of the adiabatic layer at a space velocity of the inlet gas mixture of 14,000 and 28,000 h^{-1}.

The described tendencies to limit the possibilities of using an adiabatic layer with the increase of methanol concentration in the inlet gas flow are significantly intensified with the increase of space velocity above 14,000 h^{-1}. At methanol concentrations in the inlet gas up to 0.3% a limiting factor for the upper border is once again the selectivity of the process, and for the lower border—the total degree of methanol conversion. At higher concentrations, however, the main factor is the impossibility to reach a total degree of methanol conversion of over 98.0%.

Analyzing the results presented we can conclude that the influence of the temperature, methanol concentration and space velocity of the feed gas entering the adiabatic layer on the total methanol oxidation and selectivity of the process is complex. Methanol concentration and space velocity are the most important factors. Their increase leads to rapid decrease of the borders of applicability of the adiabatic layer. Temperature influence is limited by the operating conditions of the main reactor. More often the inlet gas entering the adiabatic layer has a temperature of 270–300 °C and this fact can be corrected in a narrow border. At low inlet temperatures the limiting factor is methanol conversion, while at higher temperatures selectivity is more important.

4. Conclusions

The possibilities for optimization of the selective oxidation of methanol over oxide catalysts were studied. It was established that:

1. The increase of methanol concentration in the gas mixture fed in the reactor leads to a dramatic change both of the temperature profile of the catalyst layer and the distribution of the reaction products. The temperature of the "hot spot" rises considerably, leading to a considerable increase of the part of side reactions and to a decrease in selectivity. The increasing of the space velocity of the gas flow also leads to alteration of the temperature profile, but its influence on the reaction products distribution and the process selectivity is less pronounced. Obviously achieving optimal economic parameters of the process demands a compromise between space velocity and methanol concentration. Maintaining high productivity of the installation necessitates a maximally high space velocity in the beginning of the exploitation period of

the catalyst and reducing it in the work process at the expense of increasing methanol concentration.

2. Modification of oxygen concentration in the inlet gas mixture in the region outside the explosion region has no significant influence on the process activity and selectivity. However its decreasing below the methanol concentration leads to a displacement of the “hot spot” along the catalyst layer, and to intensifying the process of methanol dehydration to DME and decrease in selectivity.
3. The inhibition effect of water on the process of selective methanol oxidation was confirmed. It was established that the presence of 2.5–3.0% water in the inlet gas mixture is a necessary condition in the industrial realization of the process.
4. The influence of the temperature, methanol concentration and space velocity of the feed gas entering the adiabatic layer on the total methanol oxidation and selectivity of the process is complex. Methanol concentration and space velocity are the most important factors. Their increase leads to rapid decrease of the borders of applicability of the adiabatic layer. Temperature influence is limited by the operating conditions of the main reactor. At low inlet temperatures the limiting factor is methanol conversion, while at higher temperatures selectivity is more important.
5. Using an adiabatic layer under the main reactor leads in all cases to a loss of formaldehyde due to its secondary oxidation to CO. Carefully controlling the process parameters allows full compensation of these losses by the oxidation of the methanol entering from the main reactor and the secondary oxidation of DME, mainly to formaldehyde. The use of an adiabatic layer is therefore an easy and cheap way to optimize the process of selective oxidation of methanol over oxide catalysts, thus improving the quality of the obtained formalin.

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References

[1] A.P.V. Soares, M.F. Portela, A. Kinnemann, Catal. Rev. 47 (2004) 125.

[2] S.A.R.K. Deshmukh, M. Van Sint Annaland, J.A.M. Kuipers, Appl. Catal. A: Gen. 289 (2005) 240.

[3] A. Anderson, M. Hernelind, O. Augustsson, Catal. Today 112 (2006) 40.

[4] N. Pernicone, Advances and trends in the catalysis of formaldehyde production over Fe–Mo catalysts, in: M. Farinha Portela, F. Gama Freire, M. Pilar Castilho (Eds.), Meeting on Industrial and Environmental Catalysis, Lisbon, May 15–19, 1995, Actas do 38 Encontro Nacional de Cataĭ lise Baĭ sica e Aplicada (Industrial e Ambiental), Lisboa.

[5] G. Sioli, EP 0820345 B_1 (2000).

[6] G. Sioli, EP 1 166 864 A_1 (2002).

[7] SOC Italiana Resine SIR SpA 27, GB Patent 1 463 174 (1977).

[8] J.M. Tatibouët, Appl. Catal. A: Gen. 148 (2) (1997) 213.

[9] K. Ivanov, D. Dimirtov, Oxid. Commun. 31 (2) (2008) 444.

[10] R. Tesser, M. Di Serio, E. Santacesaria, Catal. Today 77 (2003) 325.

[11] K. Ivanov, BG Patent 60779 B_1 (1993).

[12] B.I. Popov, K.D. Osipova, Y.D. Pankratev, Kinet. Catal. (Engl. Transl.) 12 (3) (1971) 642.

[13] M. Carbucicchio, F. Trifiro, J. Catal. 45 (1976) 77.

[14] V.N. Bibin, B.I. Popov, Kinet. Catal. (Engl. Transl.) 10 (6) (1969) 1091.

[15] C.J. Machiels, in: A.T. Bell, L.L. Hegedus (Eds.), Catalysis Under Transient Conditions, Am. Chem. Soc. Symp. Ser. (1982) 178.

[16] P. Jiru, J.L. Tichy, B. Wichterlova, Collect. Czech. Chem. Commun. 31 (1966) 674.

[17] N. Pernicone, F. Lazzerin, G. Lanzavecchia, J. Catal. 10 (1968) 83.

[18] N. Pernicone, F. Lazzerin, G. Liberti, G. Lanzavecchia, J. Catal. 14 (1969) 239.

[19] E. Santacesaria, M. Morbidelli, S. Carrà, Chem. Eng. Sci. 36 (5) (1981) 909.