

Reductive Condensation of Acetone to Methyl Isobutyl Ketone on a Bifunctional Catalyst*

^aD. BOMBOȘ, ^bGr. BOZGA**, ^aM. BOMBOȘ, ^aA. ȘTEFAN, and ^aI. STANCIU

^aChemical Research Institute ICECHIM, 772 08 Bucharest, Romania

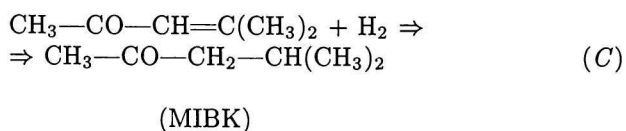
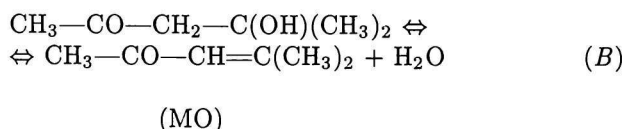
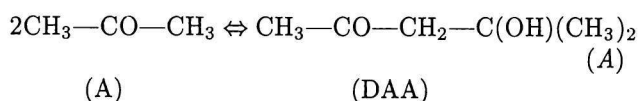
^bPolytechnical University, Department of Chemical Engineering,
772 06 Bucharest, Romania
e-mail: g-bozga@chim.upb.ro

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The methyl isobutyl ketone (MIBK) was obtained in vapour phase, from acetone and hydrogen in a single step, using Pd/(Zn) H-ZSM-5 as a catalyst. The chemical transformation occurs in a sequence of two steps, acetone condensation to mesityl oxide on the acidic sites of zeolite, followed by the mesityl oxide hydrogenation to MIBK on the palladium metallic sites.

The experiments were performed in a continuous fixed bed reactor at 0.5 MPa, 135–210 °C, hydrogen/acetone mole ratios of 0.5–9, and acetone mass hourly space velocity of 0.15–1 h⁻¹. The experimental data showed that the hydrogenation step occurs very fast compared with the condensation one, the intermediary mesityl oxide not being identified in the reaction mixture. The obtained acetone conversion was up to 55 % and MIBK selectivity between 83 % and 94 %. A kinetic model was also proposed, assuming that the overall process rate is controlled by the acetone condensation step.

Methyl isobutyl ketone (MIBK) is used mainly as organic solvent for paints and varnishes, or for the preparation of other chemical products (stabilizers, *etc.*). As a solvent, MIBK is considered environmentally friendlier than acetone, due to its lower volatility. The synthesis of MIBK from acetone consists in a three-step chemical process, including acetone condensation to diacetone alcohol (DAA), dehydration of the DAA to mesityl oxide (MO), and MO hydrogenation to MIBK



Industrially, the MIBK synthesis is performed in a single stage by direct catalytic reaction of acetone with hydrogen, on a bifunctional catalyst containing a metal (usually Pd) supported on solid acids. Presumably, the process involves the reversible condensation of acetone to mesityl oxide on the acidic sites of solid catalyst and consecutive hydrogenation of MO to MIBK on the palladium metal. As a result of different secondary reactions, a large diversity of by-products is also obtained, the nature and concentrations of which are dependent on the working conditions.

An important number of studies have been published, describing the direct MIBK synthesis from acetone and hydrogen on Pd metal, supported on ion-exchange resins [1–3], zeolites [4–7], zirconium phosphate [8], aluminophosphate [9], or niobic acid [10]. Recently, direct MIBK synthesis from acetone was reported on nickel as hydrogenation catalyst, supported on magnesia [11] or alumina [12] as condensation catalysts.

The disadvantages of the cation-exchange resin processes are the short life of the catalyst, the problem of its regeneration due to the thermal instability of the resin, higher cost of the required high-pressure system, and its tendency of polymer formation. In ad-

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**The author to whom the correspondence should be addressed.

dition, the preparation of the resin catalyst is complicated and the MIBK yield relatively low.

As compared to the Pd/resin catalyst technology, by using a highly active Pd/ZSM-5 zeolite, the process can be run at higher temperature and lower pressure, taking advantage of the high thermal stability of the inorganic oxides. Additionally, instant modification of the zeolite crystals permits suitable adjustments of the acidity and pore size, for achieving high activity and selectivity. Another advantage of zeolite catalyst support is the possibility of regeneration, by coke burning with air. The improvement of the zeolite catalyst activity is usually performed by the increase of the density of acidic sites of some particular strength, either by modifying the $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ ratio, or by promoting the zeolite with metallic oxides.

This work presents the preliminary results obtained in the gas phase of MIBK synthesis from acetone and hydrogen on a catalyst containing Pd on Zn-modified HZSM-5.

EXPERIMENTAL

The zeolite is a Zn-modified HZSM-5 (produced by ZECASIN, Bucharest, Romania). The zeolite powder was bound in an amorphous alumina matrix as extruded composite pellets, having the density 1.5 g cm^{-3} and composition 70 mass % zeolite and 30 mass % alumina. The catalyst pellets were calcined in air for 8 h at 550°C , then impregnated with Pd chloride, calcined in air for 6 h at 450°C and subsequently reduced in a stream of hydrogen at 180°C . To prevent the unfavourable interactions of metal with the acidic sites of zeolite, the Pd impregnation of catalyst pellets was performed only as a thin external shell, by spraying with an aqueous solution of palladium chloride.

The role of Zn is important in acetone condensation stage (acidity measurements by ammonia TPD method showed an increased acidity of Zn-modified ZSM-5 compared with the basic H-ZSM-5 zeolite). We tested also the activity of the catalyst obtained by impregnation of the composite pellets (H-ZSM-5 in alumina) with $\text{Zn}(\text{NO}_3)_2$ and calcination to amorphous ZnO. Adding Zn in this way, the catalyst has not evidenced any improvement in activity or selectivity. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio in the zeolite crystals was 125 and Zn mass concentration 1 % (these characteristics were furnished by the catalyst producer). The acidic centres concentration in zeolite, determined by ammonia TPD method, was 0.45 mval g^{-1} . Pd content of catalyst pellets (0.3 % by mass) was determined by a colorimetric method with samples prepared by dissolving Pd in an adequate aqueous solution. The specific surface area of the composite catalyst pellets, determined by mercury porosimetry and nitrogen adsorption measurements, was $281 \text{ m}^2 \text{ g}^{-1}$.

Acetone of anal. grade (produced by CHIMOPAR, Bucharest, Romania) and high purity hydrogen (con-

centration 99.99 %, produced by CHIMCOMPLEX, Borzesti, Romania) were used in the synthesis. A quantity of 25 g crushed extrudate, cylindrical catalyst pellets, of $1 \text{ mm} \times 1 \text{ mm}$ average dimensions, were used in all the experiments. The experiments were effected in a thermally regulated continuous fixed bed reactor. The internal diameter of the tube (catalyst bed diameter) was 25 mm and the height of the bed $\approx 70 \text{ mm}$. The catalyst bed was placed between two layers of glass beads. A thermocouple jacket of 5 mm outer diameter was also introduced in the centre of the catalyst bed in order to measure the working temperature. A cooling system maintained the temperature practically constant in the catalyst bed. The temperature was measured only in the axial direction of the bed. The measured temperature variations were under 2°C in all the experiments.

The composition analysis of the product mixture was performed by gas chromatography (HP-INNOWAX column of 30 m length and 0.25 mm inner diameter). Before the composition analysis, the reaction products were condensed and collected for 30 min in a storage vessel. Consequently, all the composition analysis represents average values over this time interval. The experiments were carried out at temperatures between $135\text{--}210^\circ\text{C}$, a constant pressure of 0.5 MPa, hydrogen/acetone mole ratios in the range 0.5–9, and mass hourly space velocities (MHSV) of $0.15\text{--}1 \text{ h}^{-1}$. Computations of liquid–vapour equilibrium for the system hydrogen–acetone–MIBK at typical reaction mixture compositions indicated that all these components are in vapour state in the working conditions. The computations based on the Peng–Robinson equation of state (for the vapour phase) and NRTL method (for liquid phase) were performed by using the thermodynamic properties library of HYSIM[®] simulator [13].

RESULTS AND DISCUSSION

To investigate the internal diffusion influence on the process kinetics, preliminary experimental runs were performed with catalyst pellets of different dimensions. Acetone conversion and product distribution, measured from experiments with extrudate pellets crushed at dimensions of $1 \times 1 \text{ mm}$, approximately overlap those obtained in the same working conditions, with extrudate pellets of $3 \times 3 \text{ mm}$. Consequently, the influence of internal diffusion on the overall process kinetics for $1 \text{ mm} \times 1 \text{ mm}$ pellet dimensions was neglected. Internal effectiveness factor values greater than 0.85, for zeolite–alumina composite catalysts in conditions close to ours, were also reported by *Hinderer* and *Keil* [14].

The effect of external mass transfer proved also to be negligible, performing experiences at different superficial velocities and constant mean contact time (constant MHSV). For our working conditions the

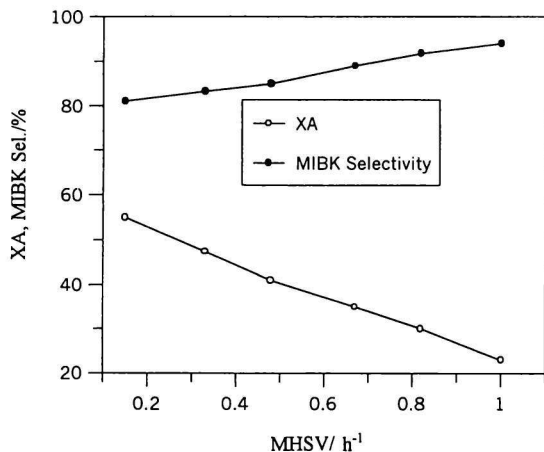


Fig. 1. Effect of the catalyst load on the process conversion and MIBK selectivity ($\theta = 135^\circ\text{C}$; $p = 0.5\text{ MPa}$; H_2/A mole ratio = 0.5).

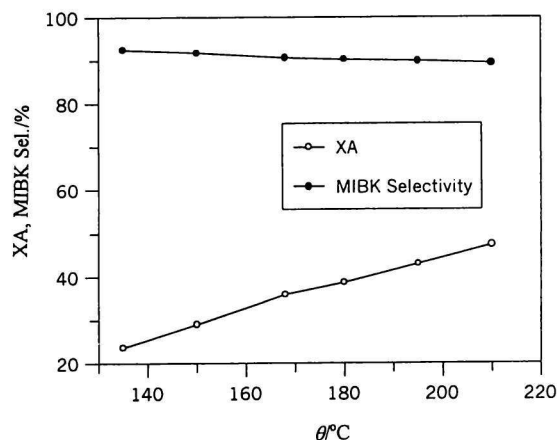


Fig. 3. Effect of the temperature on the process conversion and MIBK selectivity (H_2/A mole ratio = 1.0; $p = 5\text{ MPa}$; $\text{MHSV} = 1\text{ h}^{-1}$).

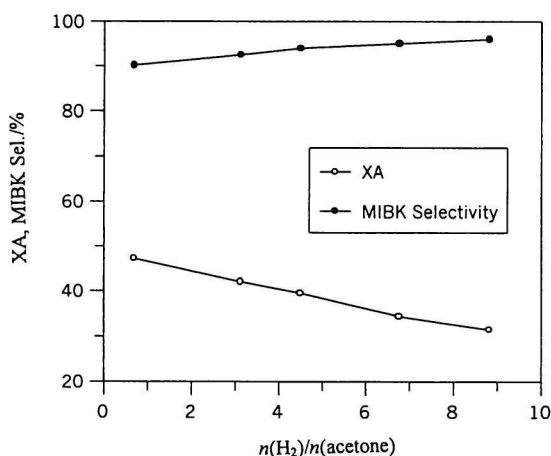


Fig. 2. Effect of the inlet mole ratio on the process conversion and MIBK selectivity ($\theta = 210^\circ\text{C}$; $p = 0.5\text{ MPa}$; $\text{MHSV} = 1\text{ h}^{-1}$).

main reaction product is MIBK. The intermediates DAA and MO were practically absent in the product mixture, which means that the hydrogenation step occurs very fast when compared with the condensation one. As by-products were identified small quantities of diisobutyl ketone, 2-methyl pentane, propan-2-ol, and traces of advanced condensation products.

During the first hours of operation after a short induction period, the catalyst activity presents a sharp decrease with time. However, after approximately two hours the deactivation intensity is very much reduced and the rate of MIBK production appears to be essentially constant. To minimize the deactivation effect, all measurements presented in the next section were effected on different charges of catalyst, after about 2 h time on-stream (the catalyst activity being considered stabilized after this operating time).

The effect of catalyst loading on the acetone conversion and MIBK selectivity is shown in Fig. 1. At low MHSV values, conversions up to 55% are obtained, corresponding to a selectivity level of $\approx 80\%$. (Selectivity is defined as the mole fraction of the reacted acetone, which was converted into MIBK.) Increasing the flow-rate of the acetone—hydrogen mixture, the conversion decreases, as expected, increasing the process selectivity.

The influence of the hydrogen/acetone ratio in the feed is shown in Fig. 2. The hydrogenation step occurring very fast, the overall process rate is not increasing by the augmentation of the hydrogen/acetone ratio over the stoichiometric value. Contrarily, by increasing the excess of hydrogen, the global rate of the process decreases due to the diminution of the acetone partial pressure. A corresponding increase of the selectivity is obtained as a result of lower intensity of secondary reactions. As observed from Fig. 2, a relatively high yield in MIBK may be obtained by an adequate selection of the reagent ratio in the feed.

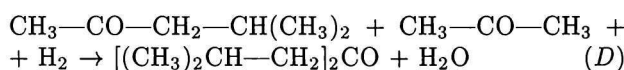
Fig. 3 shows the influence of the reaction temperature. By an increase of the temperature from 135 to 210°C, an increase of conversion from $\approx 23\%$ to $\approx 48\%$ can be realized in the conditions of a decrease in the process selectivity. The temperature dependence presented in Fig. 3 shows that there are also other influences interfering with temperature effect on the reaction kinetics. Very probably, the inhibition effect of reaction products is the main factor responsible for the dependence observed. This effect is more pregnant at conversion levels over 35–40% and could explain the fact that on the second half of temperature interval investigated the favourable influence of temperature on the process kinetics is attenuated. The presence of the mentioned inhibition effect explains also the fact that acetone conversions reported in literature for this process are generally smaller than 55%.

Process Kinetics Modelling

To represent the overall acetone transformation kinetics, it is assumed that the condensation step is rate-determining for the MIBK synthesis process. This hypothesis is supported by the absence of the DAA and MO in the reaction products. If the reaction of acetone molecules adsorbed on the zeolite surface is supposed as rate-determining for the condensation step, the following LHHW rate expression can be adopted for the three reactions represented by eqns (A) to (C)

$$v_{R1} = \frac{k_1 p_A^2}{(1 + K_w p_w + K_{MIBK} p_{MIBK})^2} \quad (1)$$

The secondary reactions occurring in the mixture are lumped in a single equation



having the rate expression

$$v_{R2} = \frac{k_2 p_A p_{MIBK}}{(1 + K_w p_w + K_{MIBK} p_{MIBK})^2} \quad (2)$$

In the relations (1) and (2), v_{R1} , v_{R2} represent reaction rates, k_1 , k_2 the reaction rate constants, K_w , K_{MIBK} the adsorption equilibrium constants for water and MIBK, respectively and p_A , p_{MIBK} the partial pressures of the same species in the mixture.

The concentration of adsorbed acetone on the catalyst surface is considered constant in all experiments due to the relatively large excess of this component in the reaction mixture (the acetone/MIBK mole ratio in the reaction mixture is superior to 2 when the acetone conversion is under 50 %). Consequently, the corresponding term was dropped out from the two rate expressions. This hypothesis was also introduced by other authors in similar kinetic studies (*Serebryakov et al.* [15], *Grigoriev et al.* [3]). The elimination of the acetone concentration term from the denominator of the main reaction rate expression has also a sound mechanistic justification. Actually, in the hypothesis introduced to infer this rate expression, the adsorbed acetone molecules do not inhibit the acetone condensation rate.

The hydrogen adsorption on the acidic sites of the zeolite was also neglected. The apparent rate constants for the main and secondary reactions, k_1 and k_2 , as well as the adsorption equilibrium constants for water and MIBK, K_w and K_{MIBK} , were estimated from the experimental data by the least-squares method. In this aim, the process was represented by the plug-flow pseudo-homogeneous model. The evolution of the reaction mixture composition along the catalyst bed is computed from the mass balance equations written in

the form

$$\frac{d\xi_{m,i}}{dW} = \frac{1}{D_m} v_{R,i}(\xi_{m1}, \xi_{m2}) \quad i = 1, 2 \quad (3)$$

$$W = 0, \quad \xi_{m,i} = 0$$

where W represents the mass of catalyst traversed by the reaction mixture, D_m the mass flow-rate, and ξ_{m1} , ξ_{m2} the intensive reaction extents of the two considered reactions (mol g⁻¹).

The partial pressures of the components are computed from the reaction extents using the common relations

$$p_j = p g_j / \left(\sum g_j \right); \quad g_j = g_{j0} + \sum_{i=1}^2 v_{ij} \xi_{m,i} \quad (4)$$

The MIBK yield has the expression

$$\eta = 2g_{MIBK}/g_{A,0}$$

and the acetone conversion

$$X_A = \frac{g_{A,0} - g_A}{g_{A,0}}$$

In the foregoing relations, p is the total pressure, g_j represents the concentration of species j in the mixture (mole g⁻¹), and $g_{j,0}$ the concentration value in the reactor feed.

The error function in the estimation procedure has the form

$$E = \sum_{l=1}^N \{ [X_{A,1}^{(c)} - X_{A,1}^{(\text{exp})}]^2 + [\eta^{(c)} - \eta_1^{(\text{exp})}]^2 \} \quad (5)$$

where $X_{A,1}^{(c)}$, $X_{A,1}^{(\text{exp})}$ and $\eta^{(c)}$, $\eta_1^{(\text{exp})}$ represent the computed and experimental values, respectively for acetone conversion (X_A) and MIBK yield (η). The minimization of the error function E in respect with the kinetic parameters k_1 , k_2 , K_w , and K_{MIBK} was performed by using the Levenberg—Marquardt algorithm [16]. The differential equations system (3) was integrated numerically by the fourth-order Runge—Kutta method. The kinetic parameter values were estimated using experimental data measured at a constant working temperature of 135 °C, 0.5 MPa, and different MHSV and inlet hydrogen/acetone mole ratios (Table 1).

The following estimation results were obtained in these conditions

$$\begin{aligned} k_1 &= 0.8303 \text{ [mol/(g catalyst h MPa}^2\text{)]} \\ k_2 &= 0.442 \text{ [mol/(g catalyst h MPa}^2\text{)]} \\ K_w &= 0.0832 \text{ MPa}^{-1}; \quad K_{MIBK} = 32.710 \text{ MPa}^{-1} \end{aligned}$$

The value of parameter K_w shows that practically only one adsorption term is important in the rate expressions, the water and MIBK partial pressures presenting closed variations. This result is also confirmed by

Table 1. Experimental Data at 135 °C and 0.5 MPa

	Acetone feedrate	H ₂ /acetone feed	Acetone conversion	MIBK selectivity	MIBK yield
	g h ⁻¹	mole ratio	%	%	%
1	14.8	0.54	37.3	83.2	31.0
2	15.4	0.75	35.5	84.3	29.9
3	15.2	1.28	35.5	86.5	30.7
4	4.1	0.5	51.5	86.5	44.5
5	5.2	1.30	52.0	83.7	43.5
6	5.3	1.70	51.1	83.0	42.4
7	33.4	0.50	23.6	92.6	21.8
8	7.1	0.50	50.3	85.1	42.8
9	10.2	0.52	46.1	87.4	40.29
10	18.63	0.51	32.7	90.5	29.6

separate experimental observations, oriented to study the MIBK and water influence on the reaction kinetics. A stronger inhibition was observed adding MIBK in initial mixture, than in the case of water. Consequently, the rate equations can be simplified to the form

$$v_{R1} = \frac{k_1 p_A^2}{(1 + K_{MIBK} p_{MIBK})^2} \quad (6)$$

$$v_{R2} = \frac{k_2 p_A p_{MIBK}}{(1 + K_{MIBK} p_{MIBK})^2} \quad (7)$$

Repeating the estimation procedure with the simplified rate expressions (6) and (7), the following values were obtained

$$k_1 = 0.8445 \text{ [mol/(g cat. h MPa}^2\text{)]}$$

$$k_2 = 0.458 \text{ [mol/(g cat. h MPa}^2\text{)]}$$

$$K_{MIBK} = 33.123 \text{ MPa}^{-1}$$

The first evaluation of the model adequacy to experimental data can be obtained from the graphs presented in Figs. 4 and 5. As observed, the relative model error is under 10 % for almost all the experiments. A single experimental point is characterized by an error value out of this range. However, we kept this point in the estimation procedure due to the scarcity of experimental data. The modelling error being randomly distributed, the quality of the fit, even not very accurate, could be considered as acceptable. The modelling results presented in this work can be further improved by increasing the accuracy and number of experimental data, as well as by using a more realistic mathematical model of the catalytic process.

CONCLUSION

The bifunctional catalyst, Pd/(Zn) HZSM-5, presents a good activity and a relatively high selectivity for the one stage of acetone conversion to MIBK. It was shown that the controlling step of the overall process rate is the acetone condensation to mesityl oxide.

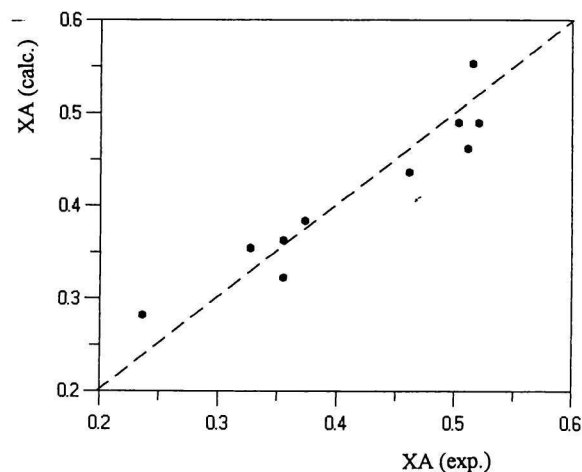


Fig. 4. Calculated vs. experimental acetone conversion values.

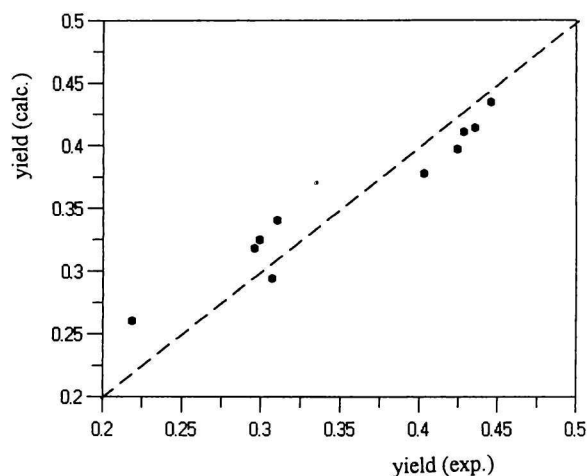


Fig. 5. Calculated vs. experimental MIBK yield values.

Also in the investigation of the process kinetics it was found that MIBK product presents a stronger inhibition effect when compared with that of the water. A simplified, isothermal kinetic model based on the

Langmuir—Hinshelwood theory was also proposed for the global acetone condensation process to MIBK.

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SYMBOLS

D_m	mass flow-rate of the reaction mixture	h^{-1}
g_j	concentration of the component j in the reaction mixture	mol g^{-1}
k_1, k_2	reaction rate constants	$\text{mol}/(\text{g cat. h MPa}^2)$
K_w, K_{MIBK}	adsorption equilibrium constants	MPa^{-1}
p, p_j	working pressure and partial pressure of the component j in the mixture	MPa
v_{R1}, v_{R2}	reaction rates	$\text{mol}/(\text{g catalyst h})$
W	mass of the catalyst	g
X_A	acetone conversion	
ξ_{m1}, ξ_{m2}	intensive reaction extents	mol g^{-1}
ν_{ij}	stoichiometric coefficient for component j in the reaction i (negative for reactants)	

Subscripts

A	acetone
MIBK	methyl isobutyl ketone
w	water

Superscripts

c	computed value
exp	measured value

Abbreviations

MIBK – methyl isobutyl ketone; DAA – diacetone alcohol; MO – mesityl oxide; MHSV – mass hourly space velocity (mass of reactant mixture feed per mass unit of catalyst and unit of time).

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