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Development of kinetic models for gas phase MTBE production

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Abstract

Methyl *tert*-butyl ether (MTBE) synthesis is nowadays carried out using resin catalysts. An alternative zeolitic catalyst is presented in this study. This catalyst presents better mechanical and thermal strength, as well as slightly better performance. It is capable of enduring temperatures that would deactivate resin catalyst. The microkinetic study presented below indicates the importance of temperature and molar feed ratio depending on the catalyst used. Activation energy was found to be 15.7 kcal/g mol. Reaction mechanism suggested involved adsorption of isobutylene on two active sites and methanol on one active site.

Keywords: MTBE; β-Zeolite; Reaction mechanism; Isobutylene; Methanol

1. Introduction

Environmental laws have induced the use of oxygenated compounds worldwide, such as alcohols and tertiary ethers, such as methyl *tert*-butyl ether (MTBE), in gasoline mixtures. Although MTBE production hit a record high in 1998 [1], several restrictions have been issued to decrease its use [2–4]. This poses a serious threat not only to MTBE production but to all other ethers' production as well. It may open the ground to heavy alcohols as octane enhancer [5]. Nonetheless, understanding ether synthesis and its mechanisms is not a subject that is near to depletion.

This ether is produced by adding methanol to isobutylene (from an olefinic gas oil cut) at temperatures between 343 and 363 K and pressures around 1.9 ± 0.3 MPa in order to keep the system in liquid phase [6–8]. The main MTBE production reaction is slightly exothermic ($\Delta H^0_{363\,K} = -10.48$ kcal/mol), therefore temperatures above 363 K do not favor equilibrium conversion at atmospheric pressure and gas phase. When the system is in liquid phase, it shows a highly non-linear behavior. In this case the best method found for predicting thermodynamic equilibrium is UNIFAC [9,10]. Nonetheless, in gas phase (0.1 MPa), a case for ideal gas could be applied as the fugacity coefficient values taken are very close to 1.

Even though, the commercial catalyst termed Amberlyst 35® is quite active for MTBE production, it shows several drawbacks: thermal instability, selectivity, which proves to be too sensitive to the reactants molar ratio (M/I), and an increase in rusting properties as temperature rises above 373 K and releases acid groups [11].

Based on the above, a promising alternative indicated in literature is the use of zeolitic catalysts, such as those based on ZSM-5 and β-zeolites. Our case is based on a catalyst developed by the Mexican Institute of Petroleum (IMP) [12], which is endowed with larger surface area, better thermal and mechanical strength, as well as higher acidity which may lead to a higher selectivity towards MTBE. A study in the gas phase

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Nomenclature

D_P	particle diameter (m)
D_R	reactor diameter (m)
E	ether (reaction mechanism)
E	activation energy (kcal/mol)
F	physical significance factor
F_i	molar flow rate of compound i (g mol h^{-1})
ΔH^0	reaction enthalpy (kcal/g mol)
I	isobutylene
k	kinetic constant
K	equilibrium constant for the reaction (atm^{-1})
K_i	adsorption equilibrium constant for substance i (ATM)
M	methanol
MTBE	methyl *tert*-butyl ether
r	intensive reaction rate
R	molar feed ratio (g mol_i/g mol_j)
R_g	universal gas constant (cal/g mol K)
S	active site (reaction mechanism)
T	temperature (K)
W	mass of catalyst (g)
$\%C$	percent conversion
$\%S$	percent selectivity
$\%Y$	percent yield

Subindexes

E	methyl *tert*-butyl ether (MTBE)
i	component i
I	isobutylene
j	component j
M	methanol
T	total
o	initial
●	adsorbed

is carried out as the basis for a future research in the liquid phase. This is done so as the basic kinetic study is easier to be analyzed.

2. Theory

Tejero et al. [13] found on resin catalysts that Langmuir–Hinshelwood–Hougen–Watson (LHHW) type mechanisms and kinetic expressions fit best experimental results.

By carrying out an in-depth analysis of the parameter interactions it was concluded that from a kinetic model of the type LHHW a surface reaction in which three active centers participate is the controlling step. These mechanisms studied involve adsorption in one center by methanol, isobutylene and MTBE, in two centers (with and without dissociation), and two molecules in one center.

After carrying out parameter fitting, thermodynamic consistency tests and activation energy calculations, model shown as Eq. (1) fitted best for Amberlyst 15®. Operating conditions were: temperature 313–335 K, $W/F_I = 0.1$–$1\ g_{cat}\ h/mol_I$, P_I=0.027–0.27 ATM and $P_M = 0.05$–0.23 ATM, $P_T = 1$ ATM.

$$r = kK_I K_M \left(P_I P_M - \frac{P_E}{K} \right) \times \left[\frac{[(1 + K_M P_M)^2 + 8(K_I P_I + K_E P_E)]^{0.5} - (1 + K_M P_M)}{4(K_I P_I + K_E P_E)} \right]^3 \quad (1)$$

Zeolitic catalysts for this kind of reaction have not been extensively studied. The work done by Chang et al. [14] is taken as one of the starting points for this study. Their experimental work was aimed at zeolitic catalysts impregnated with titania, especially on silicalite. It was found that medium or weak acid centers favor MTBE formation. The amount of acid centers is increased by addition of Ti^{4+} to the silicalite, prompting selectivity close to 100%. This was favorably compared with HZSM-5's selectivity, which includes the formation of di-methyl ether. After properly carrying out parameter fitting, with the following operating conditions: W/F_I of $4.08\ g_{cat}\ h/mol_I$, $P_I = 0.02$–0.22 ATM, $P_M = 0.02$–0.06 ATM and $P_T =$ ATM, it was concluded that model No. 6 in Table 1 best fitted the kinetic data obtained.

It is worth noting that the kinetic model that shows the best fit is in both cases the same. This indicates that the probability of being the most adequate one is high: the reaction between adsorbed methanol and adsorbed isobutylene in two different acid sites.

Table 1
Kinetic equations for zeolitic catalysts (Chang et al. [14])

Controlling step	Kinetic model	Kinetic equation
Surface reaction	1	$r = \frac{kK_I K_M (P_I P_M - (P_E/K))}{(1 + K_I P_I + K_M P_M + K_E P_E)^2}$
i-C_4H_8 adsorption	2	$r = \frac{k[P_I - (1/K)(P_E/P_M)]}{1 + K_M P_M + (K_I/K)(P_E/P_M) + K_E P_E}$
Surface reaction	3	$r = \frac{kK_I K_M (P_I P_M - (P_E/K))}{(1 + K_I P_I + K_M P_M + K_E P_E)^3}$
MTBE desorption	4	$r = \frac{kK_E (P_I P_M - (P_E/K))}{1 + K_I P_I + K_M P_M + KK_E P_I P_M}$
Surface reaction	5	$r = \frac{kK_I K_M (P_I P_M - (P_E/K))}{(1 + (K_I P_I)^{0.5} + K_M P_M + K_E P_E)^3}$
Surface reaction	6	$r = kK_I K_M (P_I P_M - (P_E/K)) \left[\frac{[(1 + K_M P_M)^2 + 8(K_I P_I + K_E P_E)]^{0.5} - (1 + K_M P_M)}{4(K_I P_I + K_E P_E)}\right]^3$

Gas phase MTBE synthesis on zeolitic catalysts at high temperatures (above 373.15 K) has been investigated by Nikolopolus et al. [15,16] as an effort to combine etherification with alcohol production from syn-gas. He found that zeolites generally present a better selectivity towards MTBE than Amberlyst 15®. It was found that the activity of zeolites with high concentration of acid sites increased with decreasing site concentration, apparently due to a lowering of neighboring sites interaction, which in term increases the strength of each individual site. Increase in activity was also attributed to the formation of aluminum extra-networks after dealuminization and thermal treatment.

Adsorption studies of these zeolites indicate that 2.5 molecules of methanol are adsorbed per molecule of isobutylene per acid site, contrasting this finding with the fact that on Amberlyst 15® it adsorbed only one molecule of adsorbate per every three acid sites on a 1:1 M/I ratio. The larger methanol adsorption rate on zeolites was attributed to a strongly protonated molecule on an Si–O–Al site.

It was also shown that excess isobutylene adsorption poisons weak acid sites due to its dimerization. As a protonating agent, methanol favors proton transfer to the olefin, making it the controlling step. This study showed that zeolites would be an adequate option to substitute resin catalysts for etherification processes.

Acidity on zeolites was also reported by Le van Mao et al. [17]. Catalyst selectivity and activity for MTBE production, are substantially modified when a superacid promoter is used to pretreat ZSM-5 and Y zeolites.

Collignon et al. [18] found that β-zeolite is as active as Amberlyst 35®, possibly due to a larger surface area compared with other zeolites. Further studies were carried out at the Mexican Institute of Petroleum [12] comparing several zeolitic catalysts with Amberlyst 35® for MTBE synthesis. Results showed a 10% higher yield for β-zeolite when compared with Amberlyst 35®. Regeneration testing at 823 K and atmospheric pressure indicated a 98% recovery to its initial activity as compared with a 21.6% loss for the Amberlyst 35®. The final catalyst composition found in this study is used for the present work. Several other works prove that β-zeolite is an adequate choice for this kind of study [19–22].

3. Experimental

3.1. Chemicals

The catalyst used is a IMP prototype based on β-zeolite (Zeolysts Intl.) and bohemite (Catapal), whose characteristics are shown in Table 2. Amberlyst

Table 2
Catalyst characterization

Catalysts	Amberlyst 35®	Zeolitic
Si/Al	–	70
Total acidity ($\mu mol_{NH_3}/g_{cat}$: 323–373 K)	1101.9	2188
Brönsted acidity ($\mu mol_{Pyr}/g_{cat}$)	518	479
Surface area (m^2/g_{cat})	50	621.5
Density (g/cm^3)	0.61 (bulk)	0.42 (packed)
Pore volume (ml_{pore}/g_{cat})	0.45	0.86
Microporous area (m^2/g_{cat})	NA	349.22
Pore diameter (nm)	24	5.56

35®'s characteristics are also shown as a basis for comparison. Pure methanol (99.99%) from Merk and pure isobutylene (99.9%) from INFRA were used. Pure nitrogen (99.998%) from INFRA was used for catalyst pretreatment.

3.2. Equipment

Experiments were carried out in a quartz tubular packed-bed differential microreactor (0.9525 cm inside diameter). Catalyst bed was about 0.95 cm in diameter and 1.5 cm in height (catalyst diluted in a 5:1 ratio with quartz). Total reactor length was about 9.85 cm to the porous plate upon which the catalyst was supported. A 60 m × 0.25 cm SPB-1 capillary column (Supelco) coupled to a Varian Star GC was used isothermally at 523 K for 30 min to analyze products on-line. Before every kinetic run, catalyst was flush for 2 h with N_2 (100 ml/min) at 383 K. Later on, the M/I feed flowed for about 30 min at operating conditions before any sampling was carried out.

3.3. Thermodynamics

This analysis was done by using the ASPEN PLUS V. 10.0 R-GIBBS module coupled with a third degree virial equation, following a study similar to that made by Abufores and Douglas [23] which uses Gibbs free-energy minimization.

From the data shown in Table 3, it can be observed, as expected, that conversion decreases with an increase in reaction temperature.

Table 3
Equilibrium constants for MTBE conversion in gas phase

Temperature (K)	K_y (1 atm)
303.15	134.92
323.15	27
343.15	6.54
373.15	1.032

4. Preliminary studies

4.1. Inert medium

The operating conditions for these tests were: T of 383.15 K, R of 0.85 g mol_M/g mol_I and W/F_I of 0.3 g_{cat} h/g mol_I. Best results after running the reaction for 5 h were obtained with quartz with a near zero conversion.

4.2. Stability tests

The operating conditions for these runs were similar to those studied by Cunill et al. [24] for Amberlyst 15®. Zeolitic catalyst (0.03 g) was diluted in quartz and evaluated at the following operating conditions: T of 343.15 K, R of 0.8 g mol_M/g mol_I and W/F_I of 0.65 g_{cat} h/g mol_I. Results for the zeolitic and commercial catalysts are shown in Fig. 1. From there it is observed that conversion using either catalyst remained steady within a period of 5 h for both catalysts. As results for Amberlyst 35® were similar to those in literature [24], the experimental set-up is considered reliable. Further testing was carried out in periods of up to 72 h without showing significant variation on the previously mentioned results.

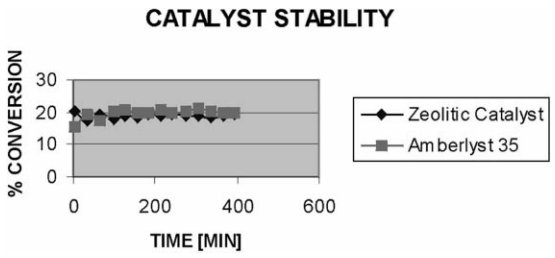

Fig. 1. Catalysts stability.

4.3. Diffusivity effects

In order to minimize heat and mass transfer effects to the inside of the catalytic particles five different catalyst samples were prepared. Results indicate that conversion remains constant for a temperature of 373 K for all particle diameters studied. It also indicates that temperature was a very significant factor to decrease intraparticle diffusion. A constant but higher value is attained with particle diameter less or equal to 0.1 mm. This is so, as the effectiveness factor tends to one when particle diameter decreases.

These observations also coincide with those made by Chang et al. [14] and Tejero et al. [13]. In both cases, for titania–silicalite and Amberlyst 15®, it was found that for particle diameters of less than 0.1 mm internal diffusion effects were negligible. It also avoids channeling and axial dispersion as with a D_R/D_P of 127 and a length of 0.3 cm experimental studies indicate [25] that it is far off from experiencing these phenomena.

In order to minimize external diffusion effects and to set an operating differential regime, further testing was carried out as indicated in Section 4.4. Fig. 2 shows some of these results. For them reaction rates could be proportional to the slopes of a fitted straight line. By selecting a maximum W/F_I of 0.5 g_{cat} h/g mol_I it was safe to expect that conversion would not go above 10% for most cases.

4.4. Experimental design

Three operating variables were of interest, temperature (T), M/I molar ratio (R), and space velocity (W/F_I). Temperatures are selected on the basis

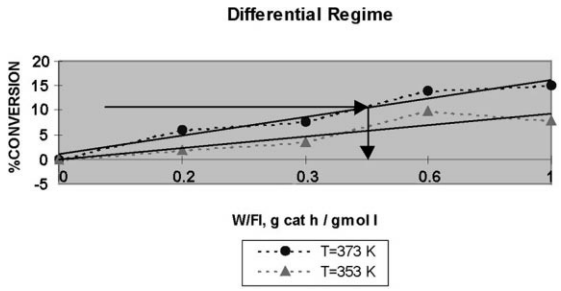

Fig. 2. External diffusion effects of zeolitic material.

Table 4
Experimental results for experimental design

No.	T (K)	R	W/F_I	%C	%S	%Y
1	333	0.7	0.1	0.9520	100.00	0.9520
2	373	0.7	0.1	11.2506	100.00	11.2506
3	333	1.7	0.1	0.1431	81.7242	0.1231
4	373	1.7	0.1	3.4747	100.00	3.4747
5	333	0.7	0.5	11.0901	100.00	11.0901
6	373	0.7	0.5	12.4066	100.00	12.4066
7	333	1.7	0.5	1.0674	100.00	1.0674
8	373	1.7	0.5	7.7824	99.2861	7.7265
9	353	1.2	0.3	1.5768	100.00	1.5768

of industrially known operating conditions, that is from 333 to 373 K, as well as for molar ratios of 0.7–1.7 g mol_M/g mol_I. Space velocity limits were chosen based on the results obtained to remain within differential regime whilst operating the reactor, from 0.1 to 0.5 g_{cat} h/g mol_I.

A 2^3 fractional factorial design with some replicates and additional points was carried out. Operating conditions for the experimental runs are shown in Table 4. STATGRAPHICS PLUS V.7 was used to carry out a stage-multivariable regression on the experimental data obtained.

Statistical model for conversion. A fitted model to explain conversion on the zeolitic catalyst was found as follows:

$$\%C = 0.14T - 6.10R + 9.88\frac{W}{F_I} \quad (2)$$

This model explains 93.47% of experimental results, has a level of physical significance (F) of 38.21 and an experimental error of 2.26%.

Further results are shown in Table 5, where it can be observed that the variables that affect conversion the most are: temperature, then molar ratio and finally space–velocity. Temperature and space–velocity do it positively, whereas molar ratio does it adversely.

Statistical model for selectivity. Selectivity for MTBE was found to follow a model where no operating variable seems to affect it. The model obtained is:

$$\%S = 97.52 \pm 5.59 \quad (3)$$

The experimental error found follows a normal distribution. An explanation for this behavior is given by the fact that selectivity itself is so high for this specific catalyst that any other parameter has no real

Table 5
Experimental runs for kinetic analysis at $W/F_I = 0.1\,g_{cat}\,h/g\,mol_I$

T (K)	R ($g\,mol_M/g\,mol_I$)	r ($g\,mol/(h\text{-}g)$)	P_Io, atm (initial)	P_mo, atm (initial)	P_I (atm)	P_M (atm)	P_E (atm)
373	0.7	1.1250	0.4529	0.3170	0.4172	0.2813	0.0356
373	1	0.6500	0.3850	0.3850	0.3599	0.3599	0.0250
373	1.4	0.4328	0.3208	0.4491	0.3069	0.4352	0.0138
373	1.7	0.3474	0.2851	0.4848	0.2751	0.4748	0.0099
353	0.7	0.6200	0.4529	0.3170	0.4332	0.2973	0.0196
353	1	0.2781	0.3850	0.3850	0.3742	0.3742	0.0107
353	1.4	0.2474	0.3208	0.4491	0.3128	0.4411	0.0079
353	1.7	0.1560	0.2851	0.4848	0.2806	0.4803	0.0044
333	0.7	0.0952	0.4529	0.3170	0.4498	0.3139	0.0030
333	1	0.0504	0.3850	0.3850	0.3830	0.3830	0.0019
333	1.4	0.0343	0.3208	0.4491	0.3196	0.4479	0.0011
333	1.7	0.0143	0.2851	0.4848	0.2846	0.4843	0.0004

impact. Temperature may not affect, as large amounts of strongly adsorbed methanol hinder the formation of isobutylene dimers.

Statistical model for yield. Model for yield was found to be:

$$\%Y * 100 = 13.23T - 595.27R + 963.28\frac{W}{F_I} \qquad (4)$$

This model follows a similar behavior as in Eq. (2). This catalyst behaves similar to the ion-exchanged resin, to the titania–silicalite and H-mordenite, but with higher selectivity. Nonetheless, its behavior is different to HZSM-5 and HY zeolites [11]. Statistical models lead to identify the impact of operating variables on the process. The experimental runs may not necessarily be considered independently as trend setters.

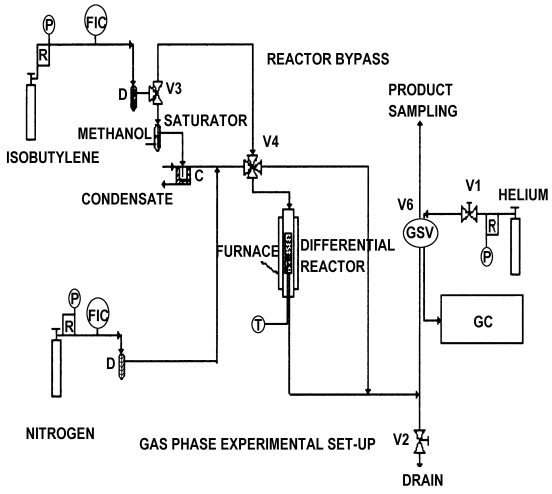

Fig. 3. Experimental set-up for gas phase etherification of isobutylene.

5. Results

Experimental data for the experimental kinetic analysis are shown in Table 5 and were carried out in the experimental set-up shown in Fig. 3.

By studying the response surface on the results obtained, it is shown that conversion increases sharply with an increase in temperature, when it happens above 348 K. When T and W/F_I remain constant, increasing R decreases conversion slightly, which is contrary to findings made by Kogelbauer and coworkers [26] for other zeolites. This may be due to differences in zeolite preparation and catalyst treatment. Comparing this catalyst with Amberlyst, it shows better performance than Amberlyst 15® and about the same as Amberlyst 35®, but with slightly smaller surface area and higher thermal strength. The most important byproducts found were diisobutylene [27].

By carrying out the appropriate simplifications in Table 1, for a preliminary kinetic analysis those equations could be reduced to simpler ones. After applying Hougen's methodology [28] for initial reaction rates, it was possible to select two equations from Table 1:

kinetic model No. 5 (Eq. (5)) and kinetic model No. 6 (Eq. (1)).

$$r = \frac{kK_I K_M (P_I P_M - (P_E/K))}{(1 + (K_I P_I)^{0.5} + K_M P_M + K_E P_E)^3} \quad (5)$$

Simplifying Eq. (5) by taking the initial rates ($P_E = 0$) the resulting equation is

$$r = \frac{kK_I K_M (P_I P_M)}{(1 + (K_I P_I)^{0.5} + K_M P_M)^3} \quad (6)$$

and Eq. (1) transforms into Eq. (7)

$$r = kK_I K_M (P_I P_M) \left[\frac{[(1+K_M P_M)^2 + 8(K_I P_I)]^{0.5} - (1 + K_M P_M)}{4(K_I P_I)} \right]^3 \quad (7)$$

Several software packages were used to solve and simplify these models: E-VIEWS® V.3 and a program based on the Buzzi-Ferraris minimization method [29]. Testing of these models was carried out by reducing the effect of several parameters as compared with the total performance of the model. Further details of these simplifications may be found in [27]. Although both equations explained data properly, after such a reduction best fit was found for Eq. (6). Following Hougen's methodology only initial reaction rates were considered, and after determining by numerical analysis that $K_M P_M \gg 1$, the simplified equation is

$$r = \frac{kK_I P_I}{K_M^2 P_M^2} \quad (8)$$

That has values for k' ($k' = kK_I K_M^{-2}$) as shown in Table 6.

Using an Arrhenius type equation ($k' = k_0\, e^{-E/R_g T}$), value for activation energy E is 15.685 kcal/g mol and k_0 is 4.734E8.

Table 6
Reaction rate constant values

Temperature (K)	k'
373	0.2361 ± 0.024
353	0.1343 ± 0.0937
333	0.02314 ± 0.00962

5.1. Reaction mechanism

Although mathematically MTBE dissociation is possible as indicated in Eq. (5), there is no evidence that such a thing may happen [30]. Therefore, the most likely mechanism to occur on the catalysts surface is defined by Eq. (7).

Adsorption. Isobutylene over two active sites,

$$I + 2S \Leftrightarrow I \bullet S_2$$

Methanol over one active site,

$$M + S \Leftrightarrow M \bullet S$$

Surface reaction. Isobutylene over two active sites reacts with methanol over one active site to yield MTBE adsorbed over two active sites and one free site,

$$I \bullet S_2 + M \bullet S \Leftrightarrow E \bullet S_2 + S$$

Desorption. MTBE desorbes to yield MTBE in the gas phase and two free active site,

$$E \bullet S_2 \Leftrightarrow E + 2S$$

Results obtained in the present work agree in most cases with several others presented in literature. Adsorption constant for methanol (K_M) is about three orders of magnitude larger than the one for isobutylene (K_I). This may be as a consequence of the rather strong adsorption of methanol on the zeolite, which inhibits overall conversion and maintains selectivity to MTBE constant. On the other hand, the value obtained for *apparent activation energy* is somewhat lower than those reported in literature (Gicquel and Torck [31] report an activation energy value of 17.005 kcal/g mol_I and Subramaniam and Bhatia [30] report a value of 18.34 kcal/g mol_I for initial rates on Amberlyst 15®).

From the results shown above, it can be proposed that isobutylene occupies two active sites and methanol fixes only on one site to carry out the etherification reaction. As methanol is more strongly adsorbed and when R is increased there is more methanol adsorbed on the surface hindering isobutylene adsorption, conversion and the reaction rate. Isobutylene adsorbs on the zeolite active sites in the same way as previously described in literature with similar compounds [32].

6. Conclusions

The zeolitic catalysts studied have shown so far, a very high selectivity in all cases (about 100%) independently of flow-rate values. This is in contrast with results obtained with the resin catalysts. Conversion increased with temperature and slightly decreased with larger R values. A simplified equation, that does not contain the dissociation term, explains the kinetic behavior of the zeolitic catalyst. Although the mechanism proposed agrees best with Eq. (7). This catalyst seems to be a promising material for MTBE synthesis.

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