DEVELOPMENT OF CONTROL SYSTEM FOR NICKEL–CONTAINING CATALYST IN DIENES HYDROGENATION

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Abstract

Based on mathematical approach method, computer modeling system was applied to dienes hydrogenation process optimization. Use of the system allows quantitative determination of sulfur consumption required for hydrogenation on nickel–containing catalyst. Research showed that the system might help to prolong catalyst life saving the desired quality of target products.

Keywords: mathematical modeling; hydrogenation; sulfuration, nickel-containing catalyst; LAB, optimal regime.

1. Introduction

Nowadays the mathematical modeling method of chemical-technological processes is intensively developing. Being effective at research and optimization of reactionary processes, the method is also widely used for optimization of industrial processes in conditions of factory practice.

The computer modelling systems, built on the basis of physical and chemical laws, are alternative to carrying out of numerous experiments. Application of mathematical modeling methods justifies itself at technological processes monitoring, at research of various types of reactors, catalysts and raw materials [1].

One of the major directions of oil refining industry is the process of synthetic washing-up liquids manufacture. In the market of synthetic washing-up liquids the leaders are anionactive detergents, the basic components of which are linear alkylbenzenes (LAB) and linear alkylbenzene sulphanates (LAS). It is caused by their high washing ability, good solubility and ecological safety.

Input for petrochemical processes complex LAB–LAS of "KINEF" Co Ltd is kerosene hydrocarbonic fraction, and the output is intermediate product for synthetic detergents production – linear alkylbenzenes (LAB) [2].

The complex includes three basic stages: dehydrogenation of higher paraffins, hydrogenation of by-products and benzene alkylation with obtained monoolefines (Figure 1).
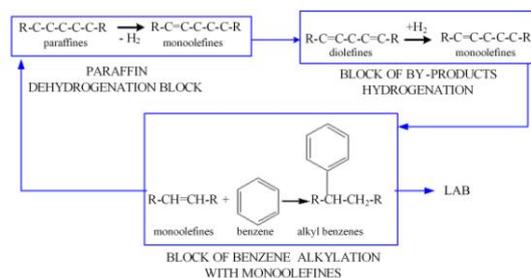

Figure 1. Technological scheme of hydrogenation unit

The operation of hydrogenation reactor is dedicated to raising the content of n–mono-olefines and lowering the content of by–products, dienes especially. Hereby the work of this reactor has a considerable impact on the whole plant output and optimal functioning, provides high production volumes for end product of desired quality.

The output and quality of alkylate depend on structure of the raw material passing through alkylation reactor, that means on   previous stages efficiency.

Optimization of hydrogenation process and research of quantitative and qualitative influence of various parameters on it is practically impossible in industrial conditions, as numerous experiments that are not favorable from the economic point of view are demanded. At the same time these problems are worth solving as fluctuations of raw material composition influence selectivity of the process.

The given problem can be solved by means of mathematical modeling methods; therefore the purpose of the present work is development of model for hydrogenation process and its application to process efficiency enhancing.

2. Experimental

2. 1 Technological bases of hydrogenation process and modeling experience

Hydrogenation in R–1401 reactor is a solution–phase process that uses nickel–aluminium catalyst. Hydrogen is solute too. Hydrogenation temperature is 180 –230 C, pressure of the process is 1.0–1.2 MPa.

The process of hydrogenation can be characterized by following features:
– chemical transformations occur in a three–phase system gas – liquid – solid (hydrogen – liquid hydrocarbons – nickel–aluminum catalyst);
– presence and normal operation of static mixer SM–1401 indicates that gas concentration in liquid is close to its equilibrium value;
– catalyst is being intentionally poisoned with sulfur compounds during the process to raise its selectivity;
– only a small part of a hydrocarbon feed stream is being converted (input mass concentration of dienes relatively to the whole hydrocarbons stream generally does not exceed 1 %, output – 0.25%).

The operation of hydrogenation reactor is dedicated to raising the content of n–mono-olefines and lowering the content of by–products, dienes especially. Hereby the work of this reactor has a considerable impact on the whole plant output and optimal functioning, provides high production volumes for end product of desired quality. However it is a complex apparatus where the conversion occurs in three–phase catalytic system. How to maintain the regime which is close to optimal is a rather complicated multiple–factor problem, and the most efficient way of solving it is mathematical modeling of the process of dienes hydrogenation on nickel catalyst subject to its deactivation by sulfur.

There are many works describing mathematical models for this important stage which proves the urgency of the task.

The work [3] describes three models for hydrogenation of dienes on nickel catalyst: Somers, Horiuti–Polanyi and model based on modified law of mass action.

Horiuti–Polanyi model was developed for ethene hydrogenation, but nowadays it is used for alkenes with different numbers of carbon atoms. According to Horiuti–Polanyi's classic mechanism, alkenes are chemisorbed on the surface of catalyst accompanied by double bond breakage and two–stage addition of dissociate hydrogen that is also adsorbed on catalyst's surface.

According to [2], desorption of monoolefines on Ni catalyst is fast and irreversible. Hereby stages of desorption cannot limit this reaction. Meanwhile it is also fast enough when using quasiequilibrium hypothesis. Therefore only the reactions on the surface can be limiting the process of hydrogenation. It is the stage of joining the first hydrogen atom to double bond of diene or monoolefine.

Thus, there is a suggestion in [4] that this stage is limiting the hydrogenation of C=C bond on Ni catalyst. There are also equations for reaction rates of dienes and monoolefines hydrogenation that depend on hydrogen and dienes concentrations.

Although there is an assumption that equilibrium constants of main reactions are temperature–independent. Since the absorption heat diminishes as the population of

surface grows, and the filled surface is usually larger in liquid phase, temperature dependence of adsorption (Vant Hoff law) is insignificant.

According to Somers model, the equation for reaction rate is rather easy and it depends on mass balance of dienes, monoolefines and paraffins. It is determined by the law of mass action under isothermal and isobar conditions [5].

In compliance with hierarchic scheme [6] chemical reaction on the catalyst grain is modeled first, and then the reaction inside the layer, and the next stage of modeling is modeling of catalytic reactor and chemical–engineering system as a whole.

In this way we made mathematical models of catalytic reforming of benzine, dehydrogenation of n–paraffins, and isomerization of pentane–hexane hydrocarbon fraction [7,8].

3. Experiment

Thermodynamic analysis of reactions on nickel catalyst of hydrogenation including deactivation by organic sulfur compounds shows that reactions of the following components can occur during the process of hydrogenation: Ni, NiS, H_2, H_2S, $C_2H_6S_2$ (dimethyldisulfide – DMDS), H_2O, CH_4, NiO. Initial data for calculating equilibrium constants [9] are given in Table 1.

Table 1 The main thermodynamic constants

Substance	ΔH^{298}	ΔS^{298}	a	$b\cdot10^{-3}$	$c'\cdot10^{5}$	$c\cdot10^{-6}$
Ni	0	29,87	16,99	29,46	0	0
NiS	−79,50	52,97	38,7	26,78	0	0
H_2	0	130,52	27,28	3,26	0,5	0
H_2S	−20,60	205,70	29,37	15,40	0	0
DMDS	−24,14	336,64	38,91	207,65	0	−73,72
H_2O	−241,81	193,82	30,00	10,71	0,33	0
CH_4	−74,85	186,27	14,32	74,66	0	−17,43
NiO	−239,74	37,99	−20,88	157,23	16,28	0

Thus, for example, at 453K (180°C) reactions have the following equilibrium constants:

$NiS + H_2O = NiO + H_2S$, $K° = 1.09\cdot10^{-7}$ (1)

$NiS + H_2 = H_2S + Ni$, $K° = 7.39\cdot10^{-5}$ (2)

$Ni + S = NiS$, $K° = 5.89\cdot10^{8}$ (3)

$C_2H_6S_2 + H_2 + 2Ni = 2NiS + 2CH_4$, $K° = 3.43\cdot10^{30}$ (4)

$C_2H_6S_2 + 2H_2 + Ni = NiS + 2CH_4 + H_2S$, $K° = 9.89\cdot10^{26}$ (5)

$H_2S = H_2 + S$, $K° = 5.89\cdot10^{-6}$ (6)

$Ni + H_2O = NiO + H_2$, $K° = 3.79\cdot10^{-4}$ (7)
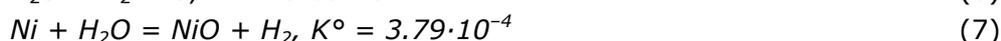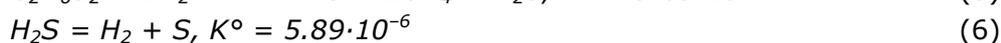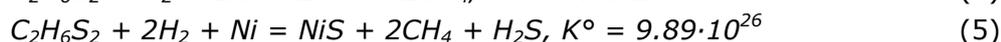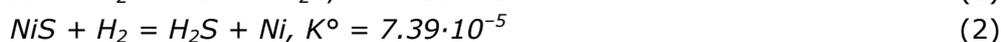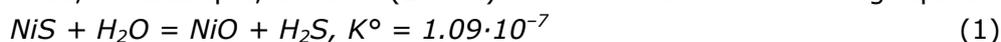
Reactions numbered 4 and 5 can be excluded from consideration since they occur instantly and irreversibly. This means that all the DMDS brought into reactor transforms into methane and S^{2-} compounds. Reactions of elemental sulfur should also be excluded, because it instantly transforms into hydrogen sulfide (reaction 6) or nickel sulfide (reaction 3).

It should be noted that the rest of reactions are linearly dependent, so the equilibrium of one of them fully depends on the equilibrium of others. Therefore the initial set of equations is simplified to the following:

$NiS + H_2O = NiO + H_2S$,

$NiS + H_2 = H_2S + Ni$.
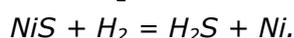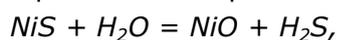
Reaction (7) shows that there can be no equilibrium with water in the system, because this equilibrium requires that the concentration of water is by three orders greater than the concentration of hydrogen. Therefore no nickel oxide (NiO) is formed in this system, and water does not impact the equilibrium.

Equilibrium concentration of DMDS relatively to hydrocarbonic feed subject to mole ratio hydrogen: dienes and temperature can be calculated using dependence of equilibrium constant on temperature (Figure 2) and initial concentrations of gases in the blend.
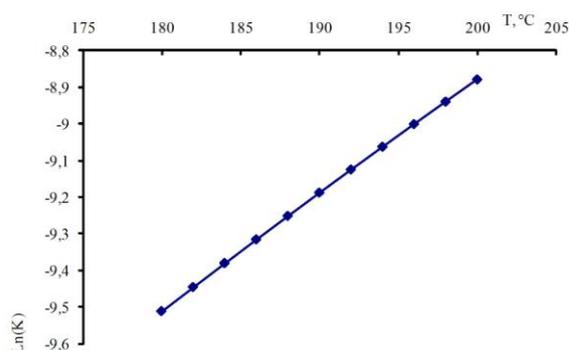

Figure 2. Dependence of equilibrium constant for reaction
of reduction NiS by hydrogen on temperature

According to equation, the amount of DMDS in ppm is:

$$x(DMDS)=2 \cdot l \cdot w(DO) \cdot K(T) \cdot 10^6 \tag{8}$$

$$w(DMDS)= x(DMDS) \, \frac{Mr(DMDS)}{Mr(HC)} \tag{9}$$

As a result of reaction network analysis and hydrodynamic regime evaluation mathematical model of the process was built. The generalized mathematical description of process is represented by system of the following differential equations of material and thermal balances:

$$G \frac{\partial C_i}{\partial z} + G \frac{\partial C_i}{\partial V} = (1 - \varepsilon) \sum_j w_j \tag{10}$$

s.c. $z=0$: $C_i=0$, b.c. $V=0$: $C_i=C_{in}$

$$G \frac{\partial T}{\partial z} + G \frac{\partial T}{\partial V} = (1 - \varepsilon) \frac{\sum_j \Delta H_j r_i}{C_p \rho} \tag{11}$$

s.c. $z=0$: $T=T_0$, b.c .$V=0$: $T=T_{in}$,
Here $z=Gt.$

4. Results and Discussion

4.1 Estimation of sulfur containing agent quantity

Using a set of equations (8, 9) allowed obtaining dependences of DMDS concentration on temperature, molar fraction and dienes content (Figures 3, 4).
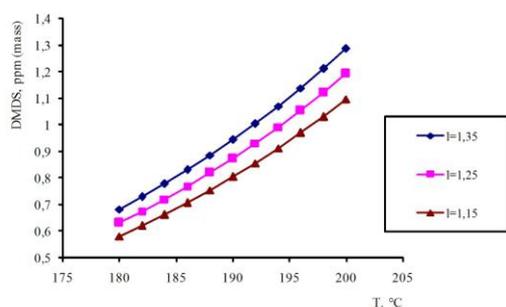

Figure 3. Dependence of DMDS amount on temperature at ω (DO) =0,6 % for different molar ratios hydrogen:dienes
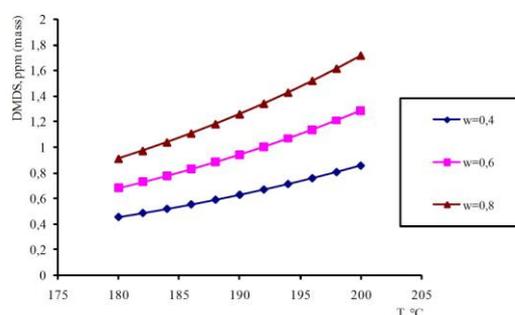
Figure 4. Dependence of DMDS amount on temperature at l=1,35 for different dienes concentrations

This diagram represents equilibrium concentrations of DMDS. If a non–equilibrium amount of sulfur is added to hydrocarbons stream, then:

– when the feed of sulfur is surplus (more than equilibrium), catalyst gradually turns into nickel sulfide till metallic nickel is present. It is proven by presence of hydrogen sulfide in the products blend after hydrogenation reactor. In this case it is necessary to decrease the sulfur feed or the catalyst will lose its activity;

– when the feed of sulfur is insufficient, nickel sulfide reduces into metallic nickel until the catalyst is completely restored, which is proven by the absence of hydrogen sulfide in the products blend of hydrogenation reactor. In this case it is necessary to raise the sulfur feed or the catalyst will lose its activity.

Thus it is necessary to add strictly the equilibrium amount of dimethyldisulfide; in this case there will be both metallic nickel and nickel sulfide providing catalyst activity rating and selectivity.

The plant in service has satisfactory dienes conversion, from 0,5–0,8 % as input to 0,1–0,2 % as output, which proves that the catalyst saves its activity in point of target reaction of hydrogenation.

There can also be observed a very little catalyst selectivity in olefines, it is even negative sometimes. For example, the change in olefines concentration in March, 2008 was from – 0,8 % to +0,6 %, avg. −0,2 %.

If adding equilibrium amount of DMDS selectivity of the catalyst on olefines can be gradually raised.

We considered hydrogenation reactor's operation in March–April, 2008. As a result of experimental data analysis it can be concluded that continuous feeding of DMDS into dehydrogenation reactor must be corrected under concentration changes of dienes coming from dehydrogenation reactor. For example, in April at almost constant parameters – t = 195 °C, sulfur feed – 1,5 ppm, molar ratio hydrogen: diolefines=1,35 – the difference between olefines concentration before and after the hydrogenation reactor varies from +0,17 % to −0,41 %, and the concentration of dienes varies from 0,51 % to 0,77 %. Obviously the feed composition, notably dienes flow rate, impact on sulfur consumption should be taken into account.

4.2. Research of sulphidation modes

Our assessment showed that sulfur feeding should be corrected when the concentration of dienes is changed as in the Table 2.

Table 2 Experimental and recommended sulfur feeding

Parameter	March					April				
Date	3	10	17	24	31	2	18	21	25	30
Experimental parameters										
Input dienes concentration, %	0,71	0,67	0,67	0,69	0,71	0,52	0,7	0,72	0,77	0,74
Reactor temperature,°C	193	194	194	195	195	195	195	195	195	195
Hydrogenous gas consumption, nm³/h	42,00	42,00	44,04	44,01	47,05	49,02	49,04	48,92	48,97	50,00
Sulfur feeding, ppm					1,5					
LAB output, t/d	176	178	178	173	172	176	150	170	174	172
Required sulfur feeding, ppm	1,46	1,44	1,57	1,61	1,7	1,78	1,76	1,79	1,79	1,84
LAB output under changed sulfur feeding, t/d	188	191	192	186	186	183	161	184	187	185

Thus adding equilibrium amount of DMDS will allow to raise monoolefines output and so the output of LAB, while the product's quality is constant because dienes level is stable and low. Average forecasted increase in olefines output is 7,0–7,6 %, and the dienes level after hydrogenation reactor is 0,1–0,19 %.

Carrying out the optimal process regime for the sulfur consumption will allow getting maximum possible olefines output and therefore LAB output. Figure 5 represents the comparison of two different sulfuration regimes for the period from 15 September, 2007 to 30 October, 2007.

Apparently, changing sulfur consumption and carrying out flexible regime leads to raising the LAB level for 2,0–6,5 %. Depending on technological parameters corrections can be made to sulfur consumption using mathematical model.

Feedstock contents should also be taken into account, particularly, dienes concentration at the hydrogenation reactor's entrance (Figure 6).
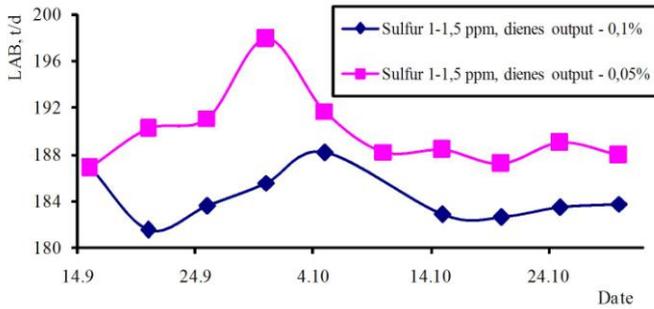
Figure 5. Different sulphidation regimes comparison
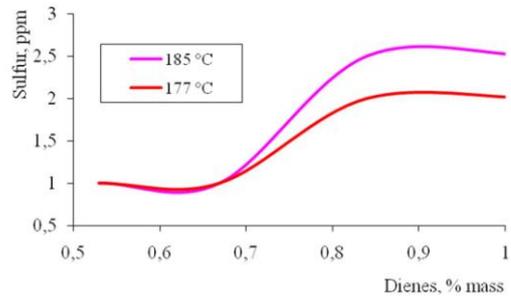
Figure 6. Required sulfur consumption in dependence on dienes concentration at the hydrogenation reactor entrance: molar ratio hydrogen: dienes=1,13, dienes after hydrogenation–0,1 % mass

The found relation (9) of sulfur concentration in hydrocarbonic blend input for reactor and molar ratio hydrogen: dienes, dienes concentration and thermal dependence of equilibrium constant laid down the foundation for modeling unit of computer control system for nickel–containing catalyst work. This system is used to calculate the optimal sulfur feeding depending on feedstock contents and technological parameters.

Figure 7 represents how the unit is working with united plant database (so called ETVD).
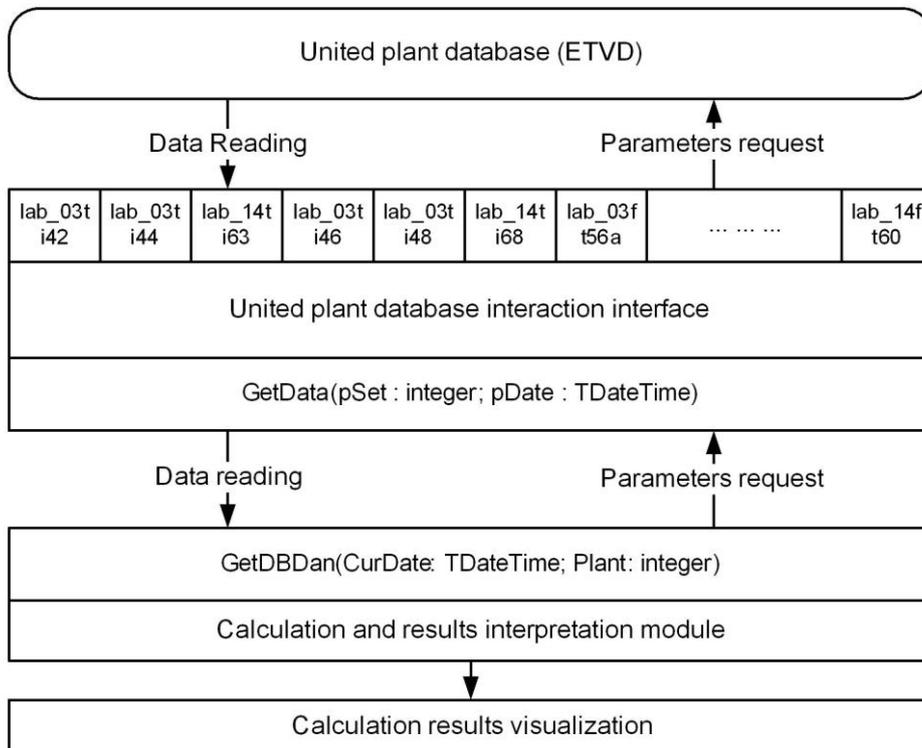

Figure 7. Scheme for connecting module use in modeling program for dienes hydrogenation on nickel–containing catalyst

It is reasonable to increase the frequency of plant products analyzing to provide possibility of continuous correction of DMDS feeding to hydrogenation reactor depending on feeding contents, technological regime and dienes concentration.

5. Conclusions

Thus, as the model takes dosed sulfuration of nickel hydrogenation catalyst into consideration, it allows quantitative determination of sulfur remains depending on reactor temperature, hydrogen consumption and feed humidity.

Working under optimal regime doesn't lead to premature catalyst poisoning, because selective sulfuration regime provides maximum catalyst productivity and meeting technological regulations in the long term.

Using of mathematical model of process allows to supervise the catalyst work and to maintain optimal concentration of DMDS in the reactor.

Symbols

H enthalpy, kJ/mole
S entropy, J/mole·K
C_i concentration of i-th hydrocarbon, mole/m^3
ε pore volume of catalyst layer
r_i rate of reaction, mol/m^3·h
w_i rate of j-th component in i-th reaction transformarion, mole/m^3·h
T temperature of the process, K
ΔH_i thermal effect of reaction, Joule/mole
C_p thermal capacity of a mixture, Joule/mole·K
P density of a mixture, kg/m^3
T_0 start temperature (temperature of an environment), K
T_{in} temperature of an input in a reactor, K
C_{in} entrance concentration of hydrocarbon, mole/m^3
V volume of catalyst, m^3
G hour expenditure of raw material, m^3/h
T time, h
Z total volume of the processed raw material, m^3
ω mass concentration of substance in hydrocarbons, % mass
x molar fraction of substance in hydrocarbons, mole/liter
l molar ratio hydrogen: diolefines, mole/mole
Mr   molar weight, kg/mole.

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