

Review  
Catalytic hydrodeoxygenation

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**Abstract**

The importance of hydrodeoxygenation (HDO) which occurs during hydroprocessing depends on the origin of feeds. HDO plays a minor role in the case of the conventional feeds, whereas for the feeds derived from coal, oil shale, and, particularly from the biomass, its role can be rather crucial. The mechanism of HDO was established using a wide range of model compounds. Complexities in the HDO kinetics have been attributed to the self-inhibiting effects of the O-containing compounds as well as inhibiting and poisoning effects of the S- and N-containing compounds present in the feeds. This is a cause for some uncertainties in establishing the order of the relative HDO reactivities of the O-containing compounds and/or groups of the compounds as well as relative rates of the removal of S, O and N. Complexities arise particularly for real feeds. This is supported by deviations from the established order such as HDS>HDO>HDN. The cases for which the overall HDN was greater than HDO were also observed. In this case, distribution of the O- and N-containing compounds in the feed and the type of catalyst are of a primary importance.

HDO is the main reaction which occurs during hydroprocessing of the bio-feeds. The current research activities in HDO are predominantly in this area. Apparently, more stable catalysts are needed to make production of the commercial fuels from the bio-feeds more attractive. © 2000 Elsevier Science B.V. All rights reserved.

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**1. Introduction**

Hydrodeoxygenation (HDO), hydrodesulphurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM) and hydrogenation (HYD) occur simultaneously during hydroprocessing of various feeds for the production of fuels. The removal of sulphur and nitrogen is environmentally driven because the fuel combustion generates SO<sub>x</sub> and NO<sub>x</sub> emissions. Also, N-compounds in the feeds poison

catalysts; therefore, their removal may be required to achieve deep HDS of fuel in a final hydroprocessing step. During HDO, oxygen in the feed is converted to H<sub>2</sub>O which is environmentally benign. Furthermore, in conventional crudes, the content of oxygen is less than 2 wt.%. Therefore, HDO requires little attention. However, in the case of synthetic crudes, such as those derived from coal and biomass, the oxygen content may be well in excess of 10 wt.%. In fact, for biomass-derived feeds, the oxygen content may approach 50 wt.%. Some of the O-compounds in the feed readily polymerize and as such are the cause of the fuel instability which may lead to poor

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performance during the fuel combustion. During hydroprocessing, such compounds may be the cause of a rapid catalyst deactivation.

The first review on HDO was published in 1983 [1]. Limited information on various aspects of HDO was available in the literature at that time. Therefore, some conclusions had to be based on the assumptions and/or on the information extrapolated from the HDS and HDN results available in the literature. At the same time, considerable interest in the upgrading of the coal-derived liquids (CDLs) was noted. This resulted in numerous studies on the HDO involving model O-compounds, mixtures and real feeds. In addition, the understanding of HDO was expanded by numerous studies on upgrading of the biomass-derived liquids, and to a lesser extent, also that of oil shale. Considering the wealth of the new information, an update of the review appears to be desirable. Thus, a database of the experimental results available in the literature can now be accessed and used to clarify several issues, i.e., effects of the catalyst type, feed composition, processing conditions etc. on HDO. The issues which require additional research may be addressed. It should be noted that HDO has also attracted attention because hydroprocessing may convert waste plastics and other O-containing wastes to usable products. Other potential applications, in which HDO can play certain role, may emerge in the future.

The H<sub>2</sub> consumption and severity of the operation required for achieving high HDO conversions depend on the content and type of the O-compounds in the feed. An active catalyst must be present to achieve desirable HDO conversions. For CDLs, more than one stage may be required to achieve complete HDO because of a high content of O-compounds and aromatics. A multi-stage operation is an essential requirement for conversion of bio-oils to commercial fuels. The first stage, the so-called stabilization stage, is performed below 573 K to remove O-compounds which readily undergo polymerization. In this case, primary reactants such as methoxyphenols, biphenols and ethers are converted to phenols which have to be removed in the second stage performed at about 623 K. Other O-compounds, i.e., ketones, carboxylic acids, esters etc. may also be involved. Furans and phenols (mostly methylated) are the predominant O-compounds in CDLs. Some of these compounds have a low HDO reactivity. Therefore, a higher H<sub>2</sub>

pressure and a higher temperature are necessary for their conversion to O-free products. On account of high phenols' content, conditions employed during the hydroprocessing of stabilized bio-oils may approach those employed during the upgrading of CDLs.

During the HDO studies, conventional hydroprocessing catalysts, such as CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub>, were used most extensively. In this review, their properties, structure and composition will receive little attention because these aspects of the catalysts have already been reviewed extensively [2–5]. The most recent account of the utilization of hydroprocessing catalysts was given by Grange and Vanhaeren [6]. The reactions which occur simultaneously with HDO, i.e., HDS, HDN and HDM, have been reviewed periodically as well. Comprehensive reviews of the reactions occurring during hydroprocessing were published by Girgis and Gates [7] and Topsøe et al. [8]. Catalyst deactivation during hydroprocessing, including the adverse effects of the O-compounds, was reviewed recently by Furimsky and Massoth [9], as well as a potential reuse of the catalysts after regeneration [10]. The aspects associated with the selection of the catalysts to match a particular feed with a reactor and hydroprocessing conditions have also received attention [11]. It is believed that advanced hydroprocessing catalysts, such as those used for deep HDS and aromatics removal, possess also a high HDO activity. In recent years, novel metal carbides and metal nitrides were successfully tested for HDO and other reactions [12]. However, it may take some time before these catalysts find a commercial use.

## 2. Oxygen compounds

Approximate compositions of feeds differing in origin are shown in Table 1. Structures of the O-compounds identified in the feeds to be used for the production of fuels are shown in Fig. 1. Thus, the feeds include conventional liquids, cracked distillates, heavy oils, fractions derived from the primary upgrading of heavy oils, CDLs, oil shale liquids and bio-oils. The proportions of the O-groups will depend on the origin of the feeds [1].

The O content of the conventional petroleum-derived feeds is less than 2 wt.% [13]. The average value of

Table 1  
Compositions of some feeds for HDO

	Conventional crude	Coal-derived naphtha	Oil shale crude	Bio-oils	
				Liquefied	Pyrolyzed
Carbon	85.2	85.2	85.9	74.8	45.3
Hydrogen	12.8	9.6	11.0	8.0	7.5
H/C	1.8	1.4	1.5	1.3	2.0
Sulphur	1.8	0.1	0.5	<0.1	<0.1
Nitrogen	0.1	0.5	1.4	<0.1	<0.1
Oxygen	0.1	4.7	1.2	16.6	46.9

the O content estimated by the American Petroleum Institute was about 0.5 wt.%. The O content increases with the boiling point of the fractions derived from petroleum. Thus, the O content of the asphaltenes and resins which were separated from the distillation residue may approach 8 wt.%. Then, while HDO re-

actions play a minor role during the hydroprocessing of light fractions, their importance increases during catalytic upgrading of heavy residues. Naphthenic acids were perhaps the first O-compounds identified in petroleum. During distillation, they concentrate in the gas oil and vacuum gas oil [14]. It has been

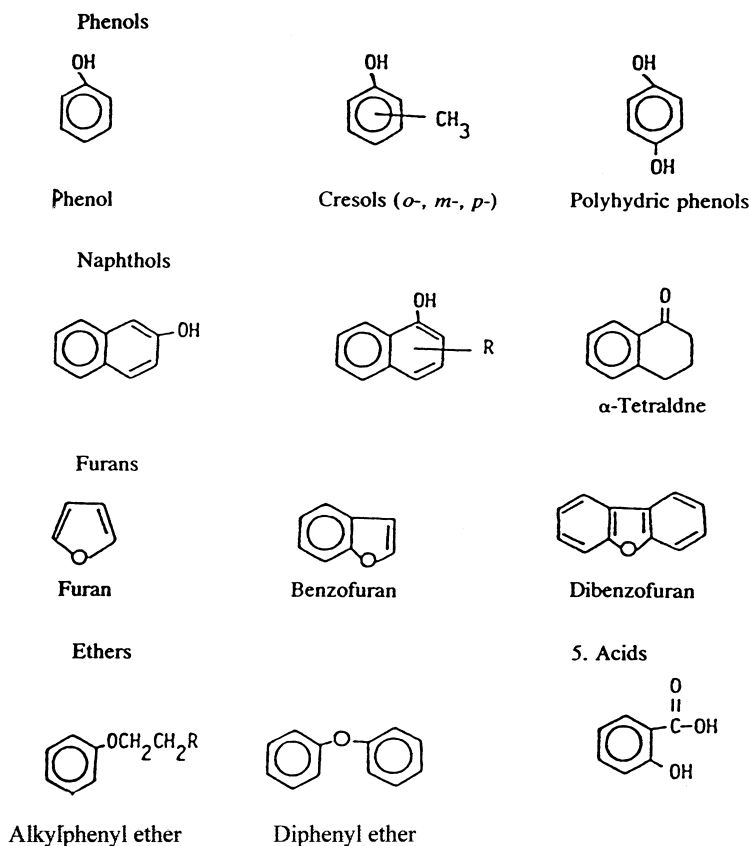


Fig. 1. Oxygen-containing compounds in petroleum.

concluded that the carboxylic acids with carbon less than C<sub>8</sub> are aliphatic. Monocyclic acids begin at C<sub>6</sub> and predominate above C<sub>14</sub>. A very small amount of the O in conventional liquids complicates the identification of the other individual O-compounds. Nevertheless, groups such as hydroxyl, carbonyl, carboxylic, etheric and sulphoxides were found in conventional fractions [1]. It is believed that at least a part of these compounds arose from the exposure to air. Thus, it is well established that such groups are formed during the autoxidation of hydrocarbons and thiophenes [15]. With respect to HDO, the most important O-compounds are phenols and furans because of their resistance to HDO. During cracking, phenols are converted to arylethers, indicating their presence in cracking distillates.

HDO is among the key reactions occurring during the fuel production from CDLs. Depending on the coal and the process, the O content in the feed may approach 10 wt.%. The type of O-compounds depends on the liquefaction process and structure of coal from which the liquids were derived as well. An extensive characterization of the CDLs from the solvent refined coal (SRC) process was undertaken by Gates et al. [16–21] for the purpose of studying the HDO reactions occurring during hydroprocessing. Using preparative liquid chromatography, these authors separated nine fractions from an SRC liquid. The O-compounds, predominantly of a phenol type, were concentrated in a very weak acid fraction and weak acid fraction containing 8.90 and 9.79 wt.% O, respectively. The following compounds were identified as major components: 5,6,7,8-tetrahydro-1-naphthol, 2-hydroxyphenylbenzene, 4-cyclohexylphenylphenol and an unidentified isomer of methylphenol. Other O-compounds, i.e., furans, ethers and ketones, were concentrated in a neutral-oil fraction. Hydroxypyridines and hydroxyindoles were found in a basic-fraction. Alkylphenols and alkylindanols were predominant components of the CDL fractions from the Exxon donor solvent (EDS) process [22]. The liquid remaining on the catalyst surface after hydroprocessing of a CDL contained arylethers, xanthenes (XA), furans and phenols [23]. Predominantly, monocyclic phenols, in addition to naphthols, indanols and fluorenols, were identified in shale oil by Bett et al. [24] and Rovere et al. [25]. Afonso et al. [26] found 1.2 wt.% of carboxylic acids in a shale oil. The

acids were linear and were, predominantly, of the C<sub>14</sub>–C<sub>20</sub> range. Species containing carboxylic groups and quinones were identified by Novotny et al. [27] and Boduszynski et al. [28], respectively.

A review of the processes used for the production of bio-oils shows a wide range of composition, although the processes can be grouped into two general groups, i.e., high pressure liquefaction and pyrolysis [29]. The O content of the primary liquids from pyrolysis may approach 50% [30], whereas that from liquefaction is less than 25% [29]. An extensive characterization of bio-oils from pyrolysis was undertaken by Maggi and Delmon [30,31]. Typical O-containing structures identified in these studies are shown in Fig. 2. Phenols may account for one-fourth of liquids derived from lignocellulosic biomass [32]. Other types of O-compounds include ketones, aldehydes, carboxylic acids, esters, alcohols and ethers [33]. Compounds containing two or more O-groups, i.e., hydroxylic and etheric groups, are quite common. Examples of such structures are guaiacols (GUAs), eugenol, vanillin and biphenols. Two steps might be required to achieve a complete conversion of such compounds to hydrocarbons. Additional phenols and dihydroxyphenols are important products of the first step, the so-called stabilizing step. Therefore, the HDO of such a species is an important part of the final step.

### 3. Thermochemical aspects of HDO

Several chemical bonds have to be broken before the final elimination of O. Some bond strengths are shown in Table 2 [34]. In the case of ethers and alcohols/phenols, the bond strength of the O attached to the aromatic carbon (C<sub>AR</sub>) is about 84 kJ/mol greater than that of the O attached to the aliphatic carbon (C<sub>AL</sub>). This implies that O elimination from phenols and aromatic ethers will be more difficult than from alcohols and aliphatic ethers. After HYD of the aromatic ring to corresponding cycloalkane, the C<sub>AR</sub>–O bond is converted to C<sub>AL</sub>–O bond. This will enhance O elimination. Then, H<sub>2</sub> pressure may be an important factor influencing HDO. Some HYD equilibria were estimated at 623 K and are shown in Fig. 3. These correlations were estimated from the following equation:

$$\log K_p = \log \left( \frac{\alpha}{1 - \alpha} \right) - m \log P$$

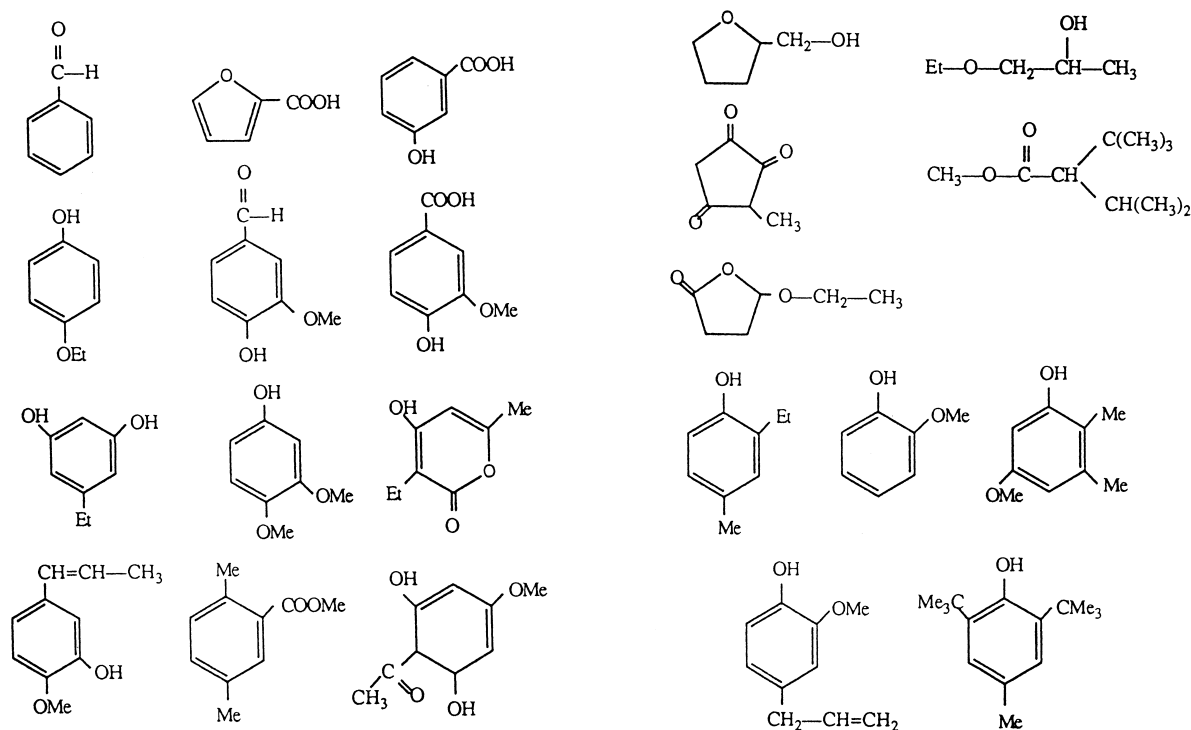


Fig. 2. Typical structures of O-compounds in bio-oils from pyrolysis [31].

where

$$\frac{\alpha}{1 - \alpha} = \frac{P_p}{P_R}$$

In these correlations,  $P$ ,  $P_p$  and  $P_R$  are pressures of  $H_2$ , product and reactant, respectively,  $\alpha$  is the conversion to hydrogenated products and  $m$  is the number

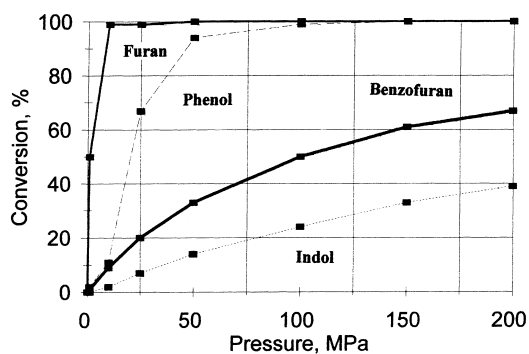


Fig. 3. Hydrogenation equilibria of model compounds.

of moles of  $H_2$ . Log  $K_p$  values for furan, phenol and indol were estimated from the thermodynamic data compilation published by Stull et al. [35] and that for benzofuran (BF) was extrapolated from the results published by Edelman et al. [36]. Being based on the ideal standard state, the calculations serve only to establish relative sensitivities of the rings to  $H_2$  pressure without paying attention to other factors, e.g., catalyst surface, steric effects etc. It is evident that the HYD of a furanic ring fused with an aromatic ring becomes more difficult. Nevertheless, after BF is converted to 2,3-dihydroBF, the strength of one C–O bond will decrease significantly. The trends established in Fig. 3 suggest that, after the ring in 2,3-dihydroBF is opened,

Table 2  
Bond dissociation energies (kJ/mol)

RO–R	339
RO–Ar	422
R–OH	385
Ar–OH	468

Table 3  
Reactions corresponding to Fig. 4 [36]

1	$\text{BF} + \text{H}_2 = 2,3\text{-dihydroBF}$
2	$\text{BF} + 2\text{H}_2 = \text{styrene} + \text{H}_2\text{O}$
3	$2,3\text{-dihydroBF} + \text{H}_2 = o\text{-ethylphenol (OEP)}$
4	$\text{OEP} + \text{H}_2 = \text{ethylbenzene} + \text{H}_2\text{O}$
5	$\text{OEP} + 3\text{H}_2 = \text{ethylcyclohexanol}$
6	$\text{OEP} + \text{H}_2 = \text{phenol} + \text{C}_2\text{H}_6$
7	$\text{Ethylbenzene} + \text{H}_2 = \text{toluene} + \text{CH}_4$
8	$\text{Ethylbenzene} + \text{H}_2 = \text{benzene} + \text{C}_2\text{H}_6$
9	$\text{Ethylbenzene} + 3\text{H}_2 = \text{ethylcyclohexane}$

the subsequent HDO of the ethylphenol intermediate will govern the overall HDO of BF.

Edelman et al. [36] determined the effect of temperature on equilibrium constants for several reactions (Table 3) which may be part of the overall HDO of BF. These correlations are shown in Fig. 4. It appears that direct HDO of BF yielding styrene and  $\text{H}_2\text{O}$  is thermodynamically more favorable than the ring HYD, although styrene is never experimentally detected under  $\text{H}_2$  pressure typically used in industrial units.

However, styrene was an important product during the HDS of the S analog benzothiophene (BT) at a near atmospheric pressure of  $\text{H}_2$  [37]. It was suggested on the basis of bond strength considerations that styrene formation from BT may be more favorable than from BF [38]. Similar evaluation of dibenzofuran (DBF) cannot be done because necessary thermodynamic data is lacking. A direct extrusion of O from DBF avoiding ring HYD is supported by the strength of the newly formed chemical bonds compared to that of the broken bonds. Thus, the dissociation energy of the  $\text{C}_{\text{AR}}\text{-C}_{\text{AR}}$  bond connecting two benzene rings in biphenyl and two newly formed  $\text{C}_{\text{AR}}\text{-H}$  bonds, i.e., about 493 and 468 kJ/mol, respectively, are among the strongest organic bonds. Also, direct extrusion may be favored by a high stability and symmetry of the final product (biphenyl). Further, the following order of the ring resonance energy was established: furan < BF < DBF [39], suggesting that HYD of the DBF will be least favorable and that of the furan most favorable. Then, the probability of the direct O extrusion will increase from furan to DBF. This approach

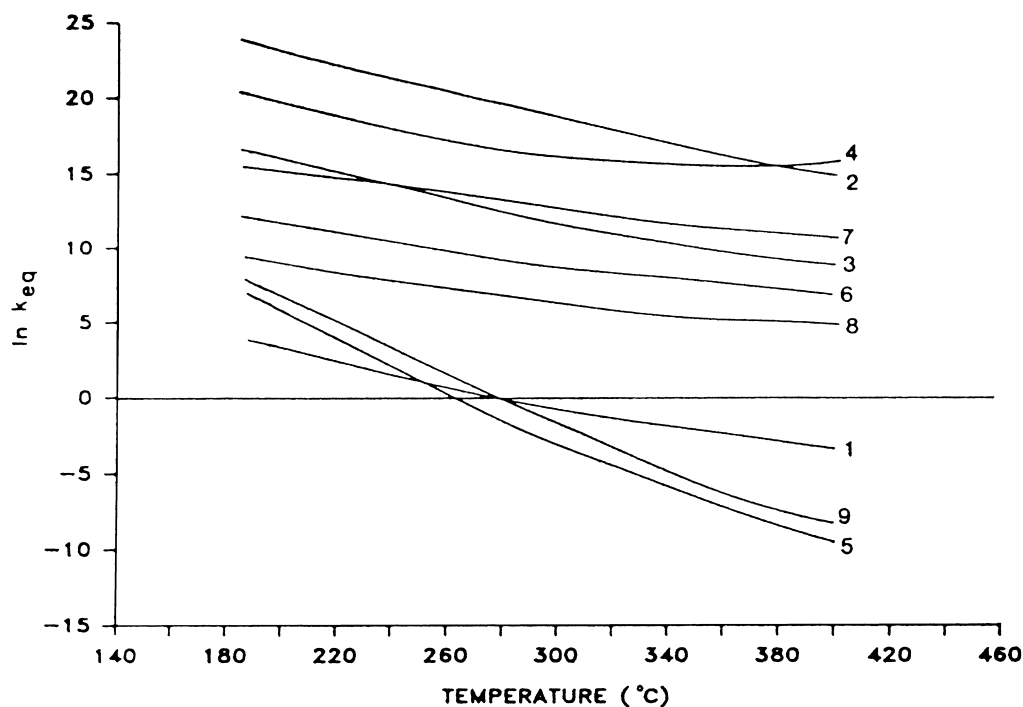


Fig. 4. Effect of temperature on equilibria constants of reaction in Table 3 [36].

was used to compare relative easiness of the removal of S, N and O from petroleum [38].

#### 4. Mechanism of HDO

Essential information for elucidation of the HDO mechanism has been obtained during studies involving model compounds. Most of the attention has been paid to furans and phenols. The latter are either present in the feed or are formed as intermediates during the overall HDO of the furans. Interests in bio-oils was the reason for including other model compounds in HDO studies, e.g., methoxy hydroxybenzenes (GUAs), dihydroxybenzenes, methylarylethers, carboxylic acids etc.

HDO occurs simultaneously with competitive reactions such as HDS, HDN, HYD and HDM, which will influence the overall HDO mechanism. Therefore, the experimental conditions employed, feed composition and type of catalyst used must be thoroughly examined before comparing the reaction networks proposed by different workers. For example, it is desirable that the feed contains enough of a sulphur donating agent to prevent modification of the sulphided form of the catalyst by H<sub>2</sub>O. Difference in the HDO mechanism can arise by comparing studies on the individual model compounds with those of mixtures of model compounds. The reactions occurring during the hydroprocessing of real feeds can be discussed in general terms only.

##### 4.1. Furans

The HDO of furan was conducted at 673 K and at near atmospheric pressure of H<sub>2</sub> in the presence of a reduced and sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst [39]. For the latter, the overall HDO conversion was more than twice that observed over the reduced catalyst. The products included ethylene, propane, propene, *n*-butane, 1-butene and *cis*- and *trans*-butenes. The yield of *n*-butane decreased with time on stream, indicating a decreased availability of the surface hydrogen due to deactivation. It was suggested that butane and butenes arose from a partially hydrogenated ring and/or HYD of butadiene, while still being adsorbed on the surface. In addition, hydrocracking of the C–C bond attached to the O heteroatom, giving C<sub>3</sub> hy-

drocarbons, was part of the overall mechanism, suggesting that CO should be among the products [41]. Chary et al. [42] compared carbon-supported CoMo and NiMo catalysts with the Al<sub>2</sub>O<sub>3</sub>-supported CoMo and NiMo catalysts at a near atmospheric pressure of H<sub>2</sub> during the HDO of furan. The HDO activity of the former was greater than that of the Al<sub>2</sub>O<sub>3</sub> supported catalysts. The products from the HDO of methyl-furan included isomers of pentene, pentane and a small amount of pentadiene [43], whereas the HDO of 2,5-dimethyl-furan yielded 1-hexenes and 1,5-hexadiene as the major products [44]. The HDO of methylfuran was severely poisoned by piperidine and to a much lesser extent also by lutidine. On account of a near atmospheric pressure of H<sub>2</sub> used, these results reflect conditions of a limited hydrogen availability, i.e., for a deactivated catalyst.

Thermodynamic equilibrium calculation revealed that, under an H<sub>2</sub> pressure which is typical for hydroprocessing, the furan ring is completely hydrogenated to tetrahydrofuran (THF) [38]. Then, the hydrogenated ring is an important intermediate before the final O elimination can take place. Under the same conditions as applied during the HDO of furan [40], i.e., a near atmospheric pressure of H<sub>2</sub>, the HDO of THF was about three times faster than that of the furan [45]. Also, butadiene was an important product, particularly over the reduced CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts. As is shown in Fig. 5, the overall HDO conversion was higher on the presulphided catalyst [46]. This was complemented by a lower coke laydown. The temperature increase from 603 to 703 K resulted in a significant increase in the butadiene yield. Other products included all the same C<sub>3</sub> and C<sub>4</sub> compounds which were formed during the HDO of furan. Kordulis et al. [47] observed that the overall HDO conversion of THF over the fluorinated NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst increased compared to the fluorine-free catalyst. However, they did not study the effect of fluorine on the product distribution. Bartok et al. [48] conducted HDO of THF over Pt catalysts supported on TiO<sub>2</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> between 423 and 623 K. The support had a pronounced effect on the selectivity. Thus, on the Pt/TiO<sub>2</sub> catalyst, the main product was butane, while on the other two catalysts, decarbonylation accompanied by CO formation was predominant. The butoxy species, still attached to the catalyst surface, was proposed to be a key intermediate for product formation. In a similar

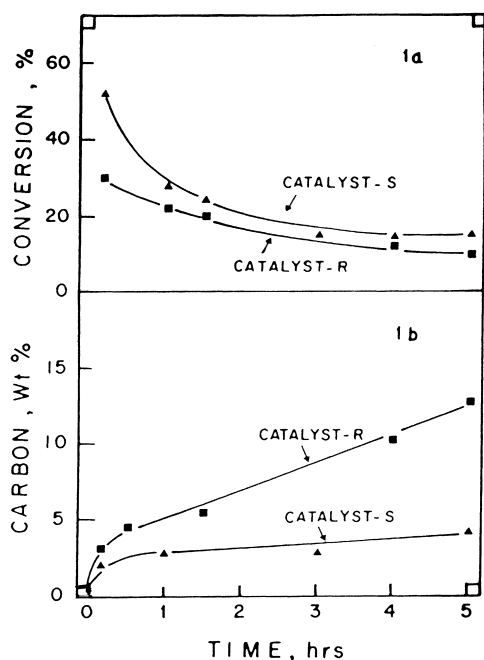
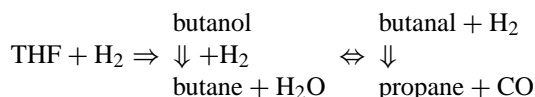


Fig. 5. Effect of catalyst pretreatment on HDO of THF and carbon deposits [46].

study published by Kreuzer and Kramer [49], the order of the catalyst activity was established as follows:  $\text{Pt}/\text{SiO}_2 < \text{Pt}/\text{Al}_2\text{O}_3 < \text{Pt}/\text{TiO}_2$ . Also, butanol was identified as a primary product which subsequently underwent either HDO to butane or decarbonylation to CO and propane. The CO product caused self-poisoning of the Pt surface, particularly that of the C–O bond cracking. Based on these observations, the authors proposed the following scheme for the reaction:



A detailed study on the HDO of BF in hexadecane over presulphided  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst (6.5 MPa of  $\text{H}_2$ ) was published by Lee and Ollis [50]. Below 533 K, 2,3-dihydroBF and *o*-ethylphenol were the only products. As the temperature was increased above 533 K, the yield of *o*-ethylphenol increased and that of the 2,3-dihydroBF decreased. Appreciable amounts of the major HDO products, such as ethylbenzene, ethylcyclohexane and ethylcyclohexene, were detected above 583 K. Traces of cyclohexane and cyclohexene

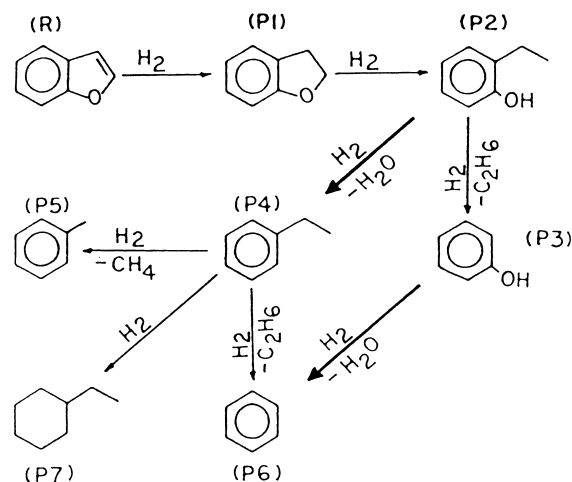


Fig. 6. Tentative mechanism for HDO of BF [36].

were also detected. The HDO of *o*-ethylphenol in the absence of BF yielded the same products as that of the HDO of BF. However, a high HDO conversion of the former was attained between 493 and 533 K, suggesting an inhibiting effect of BF on the HDO of the *o*-ethylphenol intermediate. The main steps of the reaction network proposed by Lee and Ollis [50] are in agreement with the mechanism proposed by Edelman et al. [36] shown in Fig. 6. However, the former authors observed benzene, toluene and phenol as additional, although minor, products. The slight difference may be attributed to a higher temperature, lower  $\text{H}_2$  pressure and a different catalyst ( $\text{NiMo}/\text{Al}_2\text{O}_3$ ) employed by these authors. The distribution of the main products from the HDO of BF obtained by Satterfield and Yang [51] is shown in Fig. 7. The effect of space time on the distribution is quite evident. The HDO of BF was further investigated by Ramanathan and Oyama [52] at 643 K and an  $\text{H}_2$  pressure of 3.1 MPa, using novel catalysts and one commercial  $\text{NiMo}/\text{Al}_2\text{O}_3$  catalyst. The overall HDO activities of these catalysts are shown in Fig. 8. Ethylbenzene and ethylcyclohexane were the major HDO products. The reaction network is shown in Fig. 6. Table 4 shows that, for the commercial catalyst, distribution of the products differed from that for the novel catalysts.

Lee and Ollis [53] expanded their study to include the effect of DBT on the overall HDO conversion of BF using a sulphided  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst. The



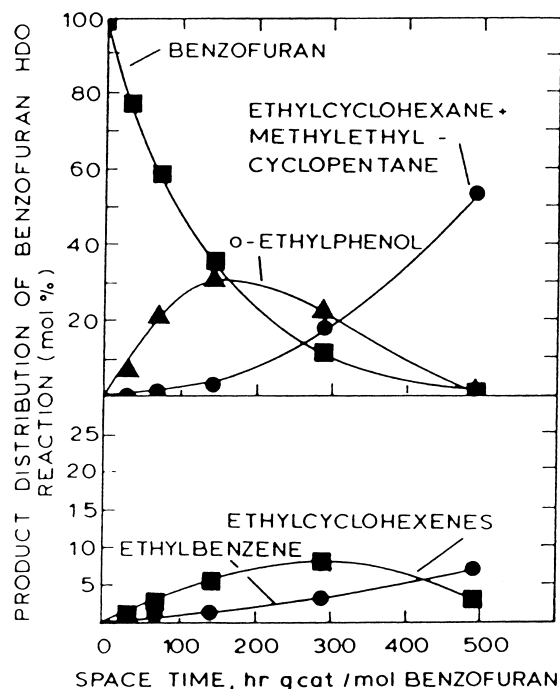


Fig. 7. Effect of space time on distribution of products from HDO of BF [51].

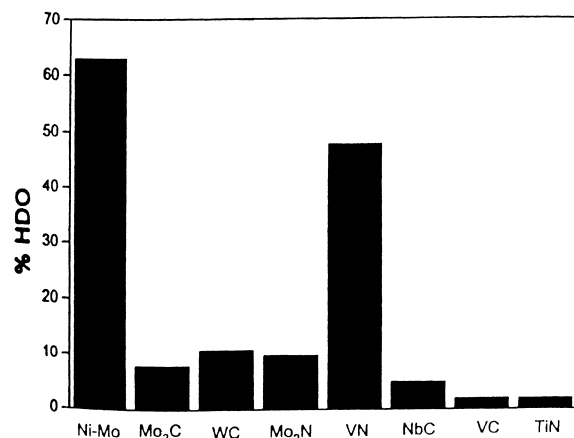


Fig. 8. Effect of catalyst type on HDO of BF [52].

Table 4  
BF conversion and selectivity (3.1 MPa; 643 K) [52]

Catalyst	BF conversion (%)	Ethylphenol (mol%)	Ethylbenzene/ethylcyclohexane
NiMo/Al <sub>2</sub> O <sub>3</sub>	69	6.1	1.2
VN	63	14.2	6.8

results in Fig. 9 show a favorable effect with increasing content of DBT until a maximum at about 0.075 mol of DBT in the mixture containing 0.15 mol BF was reached. With further increase in DBT content, the HDO rate decreased because the excess of H<sub>2</sub>S inhibited the HDO reactions. At the same time, BF had an adverse effect on the overall HDS of DBT. In contrast, over an Mo<sub>2</sub>C catalyst, the HDO conversion of BF decreased with the increasing content of DBT in the mixture [54]. Moreover, a significant change in the product distribution was observed in the presence of DBT, i.e., in the steady-state, the products included 17% ethylcyclohexane, 7% ethylbenzene, 32% 2,3-dihydroBF and 44% ethylphenol compared with 4% ethylbenzene and 96% ethylcyclohexane in the absence of DBT. Abe and Bell [55] studied the HDO of BF over Mo<sub>2</sub>N at a near atmospheric pressure of H<sub>2</sub> and observed near complete conversion to hydrocarbons at about 673 K. Products such as benzene, toluene and ethylbenzene were evenly distributed and no cycloalkanes were formed. The HDO reactions were poisoned by NH<sub>3</sub>. Poisoning and/or inhibiting effects on the HDO reactions, as well as potential surface modifications during the HDO [56] will be discussed later in the review.

Reaction routes which may occur during the HDO of DBF are shown in Fig. 10. They account for the formation of the products and intermediates observed by Krishnamurthy et al. [57] and Hertan et al. [58]. In addition, the former authors proposed the formation of 6-phenyl-1-hexanol. LaVopa and Satterfield [59] observed that the retention time of this compound coincided with cyclopentylmethyl benzene. Single-ring products, such as benzene, cyclohexane, cyclohexene etc. were the predominant products. Thus, for sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts, LaVopa and Satterfield [59] observed that more than 70% of the products (Fig. 11) had a single ring, whereas for the corresponding oxidic catalysts, the total yield of single-ring products decreased to about 25%. For the former, the single-ring product distribution is shown in Table 5. Girgis and Gates [60] also concluded that formation of the single-ring compounds (cyclohexane, benzene and methyl cyclopentane) was the most rapid pathway for the HDO of DBF. Thus, the assumption that cyclohexylbenzene and biphenyl are the only products of the HDO of DBF gave a steadily decreasing mass balance

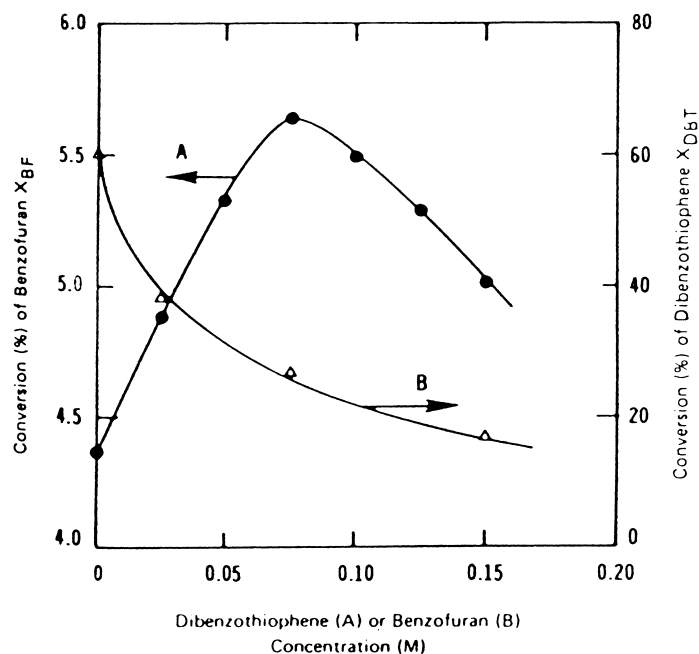


Fig. 9. Effect of DBT on HDO of BF and BF on HDS of DBT [53].

closure with increasing DBF conversion. Fig. 12 shows that the mass balance closure could be obtained only by assuming that the single-ring products accounted for the difference. It can be questioned whether single-ring products arose directly from the parent reactant or were formed in secondary reactions of the hydrogenated intermediates. The latter route is preferred on the basis of the product distribution

from the HDO of phenylphenol and cyclohexylphenol observed by LaVopa and Satterfield [59]. As Fig. 13 shows, the HDO of 2-cyclohexylphenol gave about 90% single-ring products compared to less than 20% for the HDO of the phenylphenol. Cyclohexane accounted for about 80% of the single-ring products. The profiles in Fig. 13 suggest that dicyclohexyl was a precursor to cyclohexane formation.

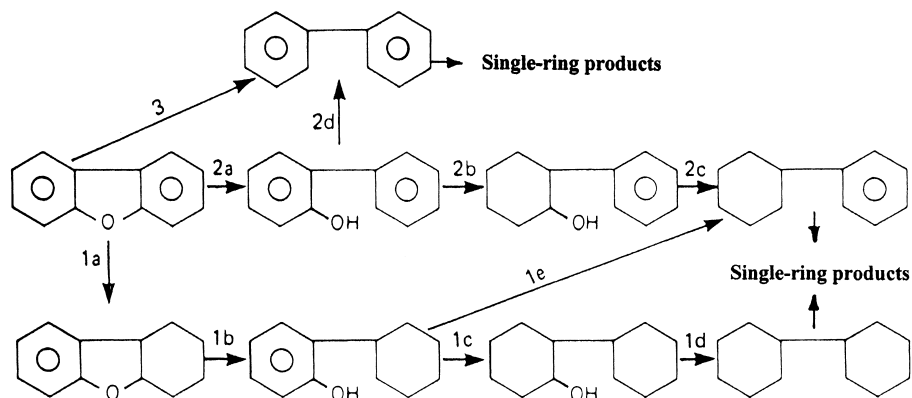


Fig. 10. Mechanism of HDO of DBF.

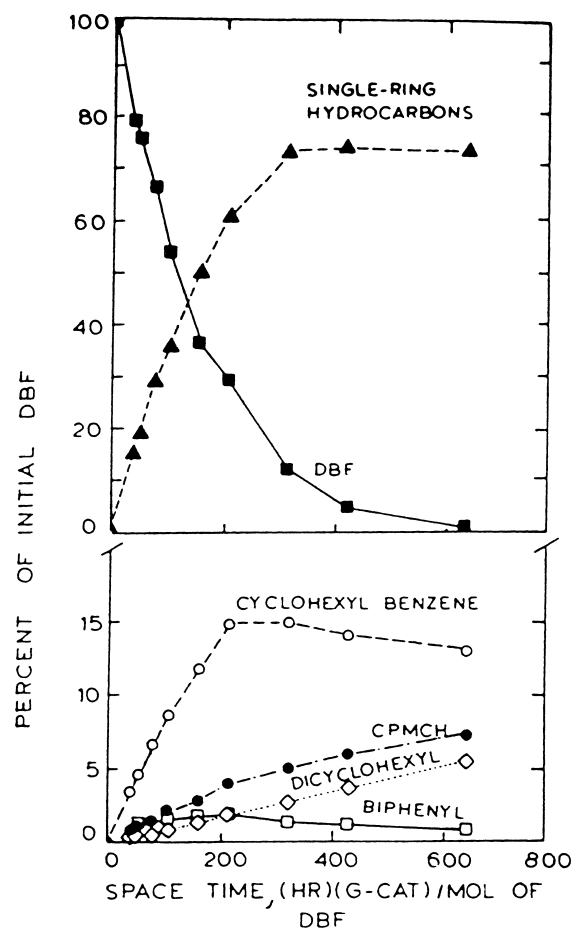


Fig. 11. Effect of space time on distribution of products from HDO of DBF [59].

Table 5

Selectivity towards single-ring products on sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts<sup>a</sup> [59]

Compound	% Selectivity	
	CoMo	NiMo
Cyclopentane	7.1	7.0
Methylcyclopentane	6.6	9.0
Cyclohexane	47	50
Methylcyclohexane	2.5	2.5
Cyclohexene	<sup>b</sup>	<sup>b</sup>
Benzene	3.3	3.6
Total single-ring products	71	72

<sup>a</sup> Note that the selectivities are identical for both catalysts.

<sup>b</sup> Varies.

#### 4.2. Phenols

The substituted phenols are predominant phenolic compounds. The effect of substitution on the overall HDO conversion was investigated by Rollman [61]. Odebunmi and Ollis [62] studied the HDO of cresols in the presence of aged and fresh sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts in low temperature range (498–548 K) and high temperature (623–673 K) range and an H<sub>2</sub> pressure ranging between 3.0 and 12.0 MPa. In a continuous microreactor, they established the following order of HDO reactivity: *meta*>*para*>*ortho*. Toluene and cyclohexane were the main products. Small amounts of methylcyclohexene were also formed. At low temperatures and on the freshly sulphided catalyst, toluene was the primary product which was subsequently hydrogenated to methylcyclohexane. At high temperatures and on the aged catalyst, the subsequent HYD of toluene disappeared and was replaced by the formation of methylcyclohexane directly from the cresol adsorbed on the catalyst surface. In subsequent studies, Odebunmi and Ollis [63,64] observed inhibiting effects of indole, as well as BT and DBT, on the overall HDO; however, distribution of the HDO products remained unchanged. While using an Ni–Cr catalyst, Samchenko and Pavlenko [65] observed that *o*-methyl and *p*-methylphenol were more stable than phenol and *m*-methylphenol. The following sequence of decreasing HYD rate was established by Shin and Keane [66] over an Ni/SiO<sub>2</sub> catalyst: phenol≈*m*-cresol>*p*-cresol>*o*-cresol, suggesting that the steric effect of *o*-substitution is important regardless of the type of catalyst [67]. The adverse effects of *o*-substitution on HDO were confirmed by Gevert et al. [68], who investigated a series of methyl-substituted phenols in the presence of a sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. Their experiments were performed in a batch reactor at 573 K and an H<sub>2</sub> pressure of 5 MPa. The products formation during this study is shown in Fig. 14. Thus, small amounts of methylcyclohexene were formed initially; however, it was gradually converted to methylcyclohexane. This suggests that methylcyclohexene is a precursor to the formation of methylcyclohexane.

A series of *o*-substituted phenols was investigated by Furimsky et al. [69] using oxidic and sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts. The overall HDO conversions of the phenol, *o*-*tert*-butylphenol and *o*-ethylphenol,

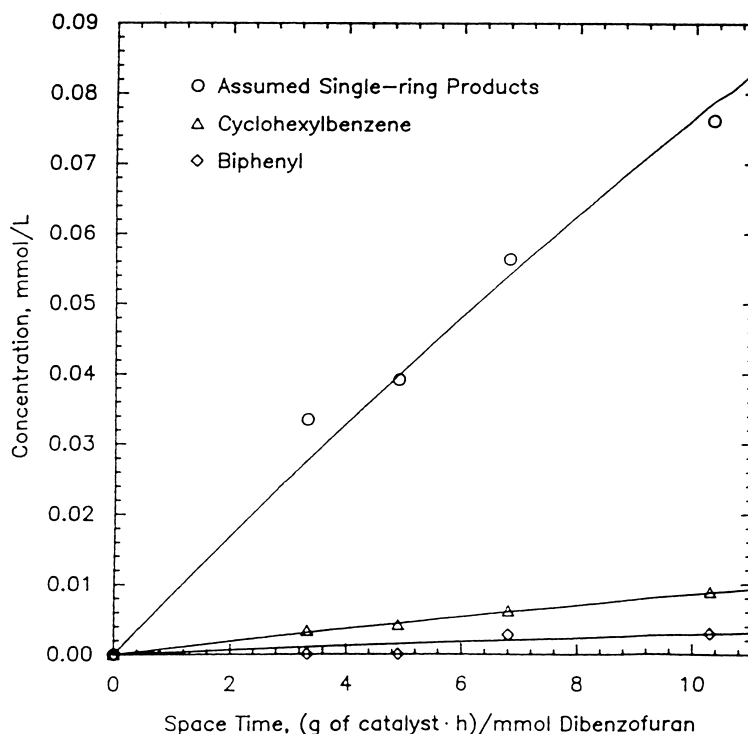


Fig. 12. Effect of space time on formation of two-ring products from HDO of DBF [60].

were similar. As expected, di-*o*-methylphenol was the least reactive and it underwent a greater dealkylation than *o*-methylphenol. The catalyst presulphiding had a pronounced effect on the product distribution, particularly on the yield of the hydrogenated parent product. *tert*-Butylphenol was completely dealkylated to benzene and cyclohexane. Thus, its HDO involved that of the phenol. Benzene rings containing one more methyl group than the parent reactant were also detected, although in small quantities. Similarly, 2,6-*tert*-butyl-4-methylphenol was completely dealkylated in both 2,6-positions, whereas the 4-position remained unchanged [70]. The overall mechanism for the HDO of the *o*-substituted phenols shown in Fig. 15 includes two main HDO reactions, i.e., direct HDO and HDO via hydrogenated phenol, occurring in parallel. In the latter case, H<sub>2</sub>O elimination may result in the formation of the intermediate methylcyclohexene species, which will be hydrogenated rapidly. The formation of cyclohexene, alkylcyclohexenes and methylcyclopentanes is also shown in Fig. 15,

although these were only minor products. Very small quantities of these products were detected by Laurent and Delmon [71] and other workers, particularly at high reactant conversions.

A study on the HDO of cresols, published by Wandas et al. [72], was conducted in the presence of naphthalene over a CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst at 633 K and 7 MPa of H<sub>2</sub>. Conversion of cresols in the presence of naphthalene was lower than that of cresols reacting individually. Also, in the former case, a considerably greater variety of compounds was formed in addition to methylcyclohexane, toluene and ethylcyclopentane, which were the main products during the HDO of single cresols. New products included cyclohexane, dimethylcyclohexanes and xylenes (mainly *m*-xylene in the case of *o*- and *p*-cresols), as well as the O-containing intermediates such as phenol, *o*-cresol arising from *p*-cresol, dimethyl and even trimethylphenols. Thus, in the case of *o*-, *p*- and *m*-cresols, the predominant species were 2,6-dimethylphenol, 2,4-dimethylphenol and

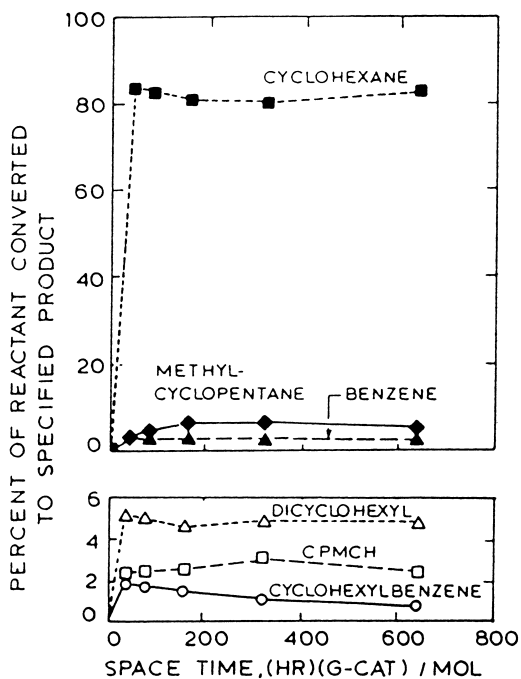


Fig. 13. Effect of space time on distribution of products from HDO of 2-cyclohexylphenol [59].

2,5-dimethylphenol, respectively. The predominance of *m*-xylene in the case of *o*- and *p*-cresols, i.e., arising from 2,6- and 2,4-dimethylphenol, was noticed. The tentative mechanism depicting these reactions pro-

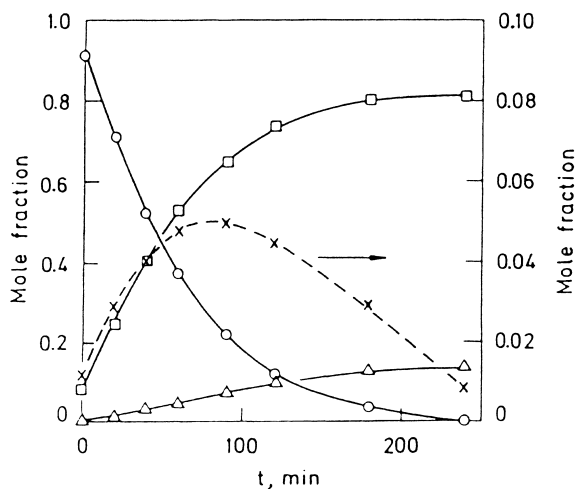


Fig. 14. Distribution of products from HDO of 4-methylphenol. ○: 4-methylphenol; □: toluene; △: methylcyclohexane; ×: methylcyclohexene [68].

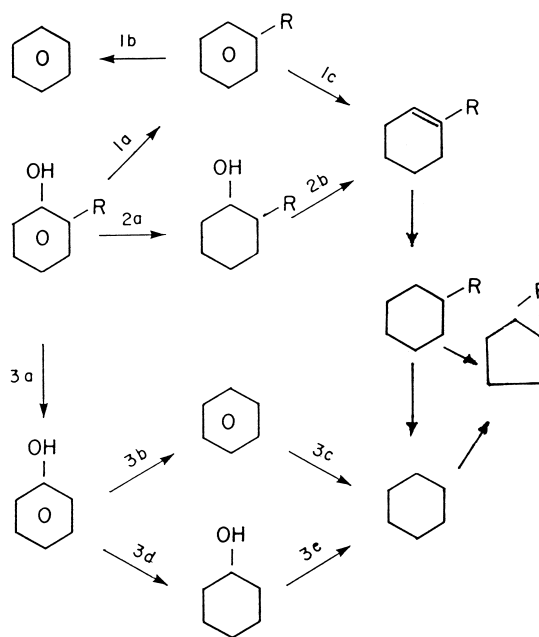


Fig. 15. Mechanism of HDO of 2-methylphenols.

posed by Wandas et al. [72] is shown in Fig. 16. The much lower yield of tetralin in the presence of cresols compared to pure naphthalene was attributed to a hydrogen transfer from tetralin to phenols. Methyl-naphthalene and methyltetralin were also observed among the products. Participation of the hydrogen donors during HDO received little attention, although the high reactivity of the fused aromatic rings to HYD, observed by Girgis and Gates [60], may suggest that hydrogen transfer from a donor formed as an intermediate to an O-compound may be part of the overall HDO mechanism.

The product distribution shown in Fig. 17 was the basis for the reaction network of the HDO of naphthal in Fig. 18, proposed by Li et al. [73]. This network

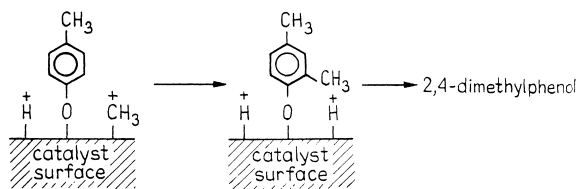


Fig. 16. Mechanism of formation of xylenols from cresols [72].

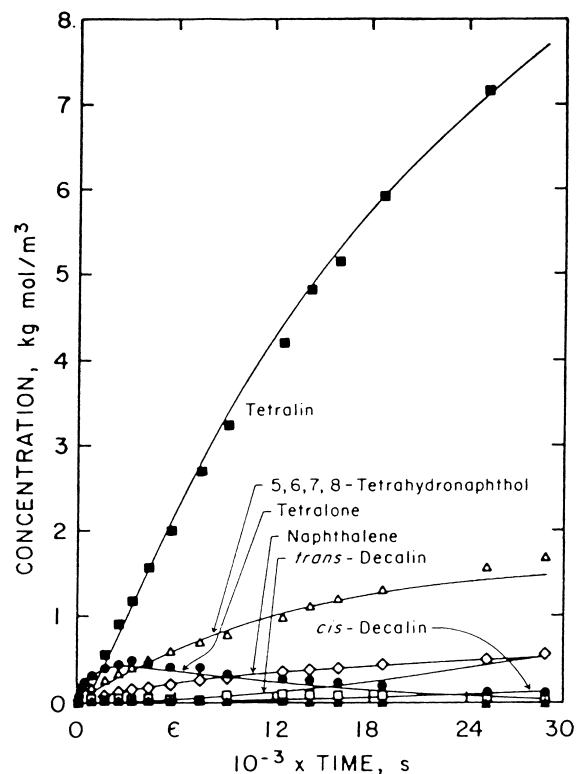


Fig. 17. Product distribution from HDO of naphthol [73].

shows that tetralone reaches a maximum, indicating its conversion to other products. The work was conducted in the presence of a sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst at 473 K and 3.5 MPa of H<sub>2</sub>. At this temperature, HYD of aromatic ring is the preferred route, compared to the direct HDO of naphthol. Thus, tetralin and 5,6,7,8-tetrahydro-1-naphthol account for most of the converted naphthol. However, direct HDO of naphthol exceeded ring HYD at higher temperatures. It was proposed that a keto-enol conversion involving 1,2-dihydronaphthol and tetralone was part of the network. Also, the rates of formation of *cis*- and *trans*-decaline were very low. Vogelzang et al. [74] compared the sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst with its oxidic form and observed that the former accelerated routes 1 and 3, whereas the oxidic form increased the rate of route 2 in Fig. 18. Girgis and Gates [75] observed that, at 623 K, 5,6,7,8-tetrahydro-1-naphthol was rapidly converted via two routes, i.e., one giving tetralin and the other octalins. They postulated that

some octalins were formed from the perhydrogenated intermediate, i.e., 1-decalol. These authors proposed that octalins can be converted to tetralin and even naphthalene. This was the simplest assumption giving a good representation of the data. In such a case, intermediate tetralins and octalins may act as hydrogen donors. Tentative mechanism for the HDO of 5,6,7,8-tetrahydro-1-naphthol proposed by Girgis and Gates [75] is shown in Fig. 19. It involves initial HYD of the reactant via protonation at the ring containing the OH group, followed by hydride addition. The latter forms a cyclic diolefin, which may react either via rapid HYD to give decalol or dehydrogenation to give tetraline. Curtis and Pellegrine [76] used a soluble Mo naphthenate to study the HDO of naphthol in a batch reactor. At 653 K and an H<sub>2</sub> pressure of about 8.8 MPa, these authors observed tetralin as the major product and naphthalene and decalin as minor products, whereas the hydrogenated naphthols were not observed.

Lee and Satterfield [77] studied the HDO of 8-hydroxyquinoline on a sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst at 633 K and 6.9 MPa pressure of H<sub>2</sub>. The reaction network included three routes. Route 1 was HYD to 8-hydroxy-1,2,3,4-tetrahydroquinoline, followed by complete HYD to 8-hydroxy-decahydroquinoline which underwent C–O hydrogenolysis to decahydroquinoline. Route 2 involved the HYD of C–O and hydrogenolysis to give 1,2,3,4-tetrahydroquinoline. Route 3 leads to 8-hydroxy-5,6,7,8-tetrahydroquinoline followed by removal of the OH group to yield 5,6,7,8-tetrahydroquinoline. The HDN reactions occurred only after HDO was completed. Thus, the overall hydroprocessing of the reactant was governed by the rate of HDN. A mechanism involving tautomerism was proposed by Kim and Allen [78,79] for the HDO of pyridonols and chloropyridonols in the solution of pyridine over a sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst between 548 and 598 K and 10.5 MPa of H<sub>2</sub>.

#### 4.3. Ethers

Arylethers are of primary interest because of their high stability as given by a much greater bond strength of the C<sub>AR</sub>–O bond compared to the C<sub>AL</sub>–O bond (Table 2). Thus, dibenzylether reacted completely even in the presence of poison, such as quinoline

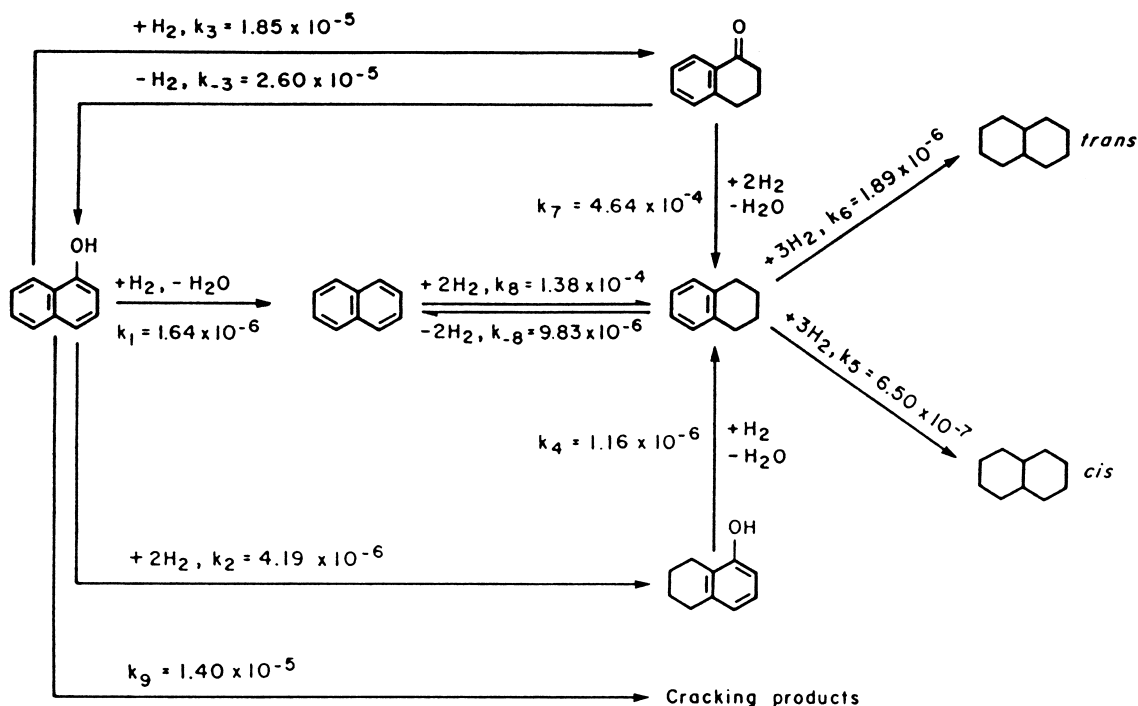


Fig. 18. Product of HDO of naphthol [73].

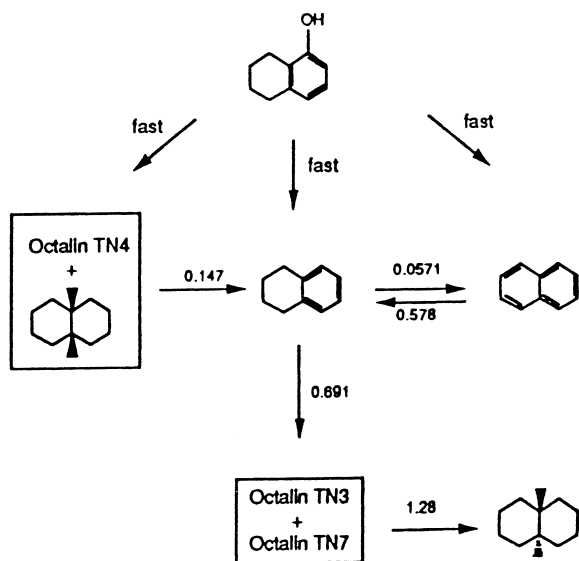


Fig. 19. Mechanism of HDO of 5,6,7,8-tetrahydronaphthol [75].

[50]. Artok et al. [80] compared dinaphthylether with diphenylether between 648 and 698 K and at an  $H_2$  pressure of 6.9 MPa in the presence of  $MoS_2$ . HDO of the former involved HYD of the substrate and O-containing intermediates, followed by direct dehydroxylation. However, in the case of the diphenylether, the formation of benzene and phenol occurred initially. The HDO was completed by converting phenol to benzene and cyclohexane, and isomerization of the latter to methylcyclopentane. Similarly, Petrocelli and Klein [81] identified phenol and benzene as primary products during the HDO of diphenyl ether over a sulphided  $CoMo/Al_2O_3$  catalyst at 7.0 MPa of  $H_2$ . At higher conversions (above 573 K), phenol was converted to benzene and cyclohexane (Fig. 20), in agreement with the study published by Shabtai et al. [82]. Kirby et al. [70] studied the HDO of dinaphthyl ether and XA in the presence of an organometallic  $CoMo$  precursor. The former was more reactive, i.e., at 673 K, conversion of the dinaphthyl ether and XA was 100 and 58%, respectively. Dinaphthyl ether yielded tetralin and naphthalene as major products,

whereas for the latter, various phenols accounted for most of the converted reactant.

#### 4.4. Bio-oil compounds

Fig. 20a was added to assist the reader with the uncommon structures of O-compounds used frequently to study the HDO mechanism of bio-oils. They include dihydroxyphenols, alkyl-arylethers, ketones, carboxylic acids, esters and alcohols. In most studies, conventional hydroprocessing catalysts have been used. Some of these compounds readily polymerize to coke-like products, even during their distillation. Then, a stabilization step, usually performed between 473 and 573 K, may be required, particularly if a prolonged storage of such liquids is anticipated [83–93]. Most of the studies involving these compounds focussed on the stabilizing step only, i.e., phenols were the major O-containing products. Then, the HDO of

the stabilized liquids can be described in terms of the HDO of phenols.

Guaiacol (GUA) and substituted GUAs (Fig. 20a) have attracted much attention because of their relatively high content in bio-oils and low stability. The mechanism shown in Fig. 21 indicates coke formation [90]. Coke was formed from both GUA and the primary product catechol (CAT). This is clearly shown in Fig. 22. Thus, a mass balance closure could not be achieved. The reaction network proposed by Delmon et al. [84,85] and Bredenberget al. [86–88] over a CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst considers the hydrogenolysis of the methoxy group to CAT and methane as the first stage, followed by the elimination of one OH group from CAT in the second stage to produce phenol. The coke arises from the interaction of GUA with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support rather than with the active metals [85]. CAT gave a similar amount of coke as the latter when treated under the same conditions separately.

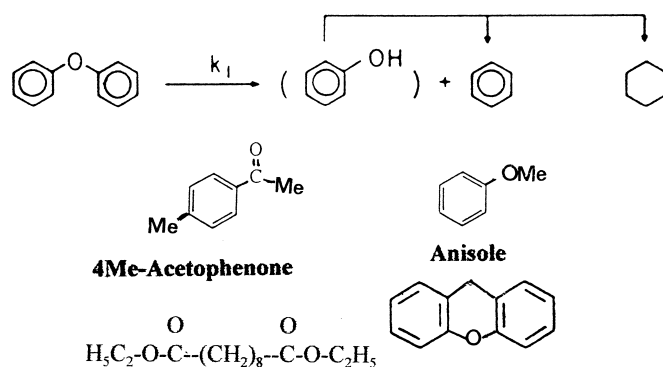


Fig. 20. Mechanism of HDO of diphenylether [82].

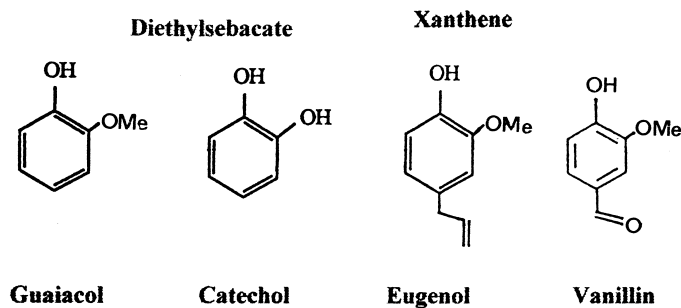


Fig. 20a. Some uncommon structures discussed in the text.



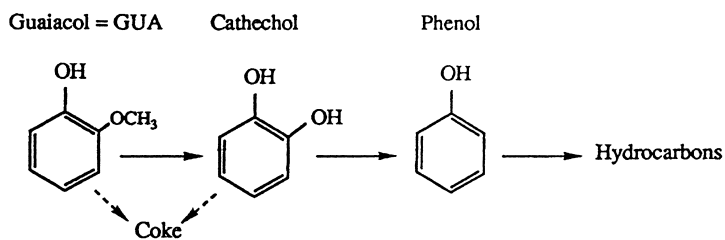


Fig. 21. Mechanism of HDO of guaiacol [90].

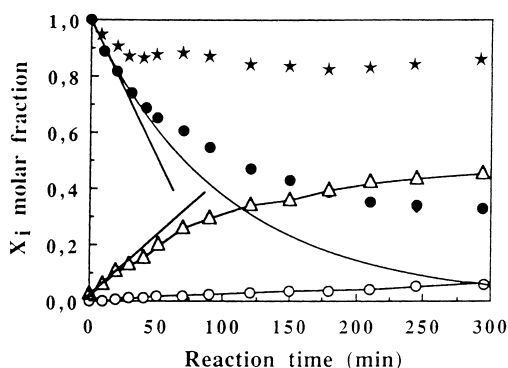
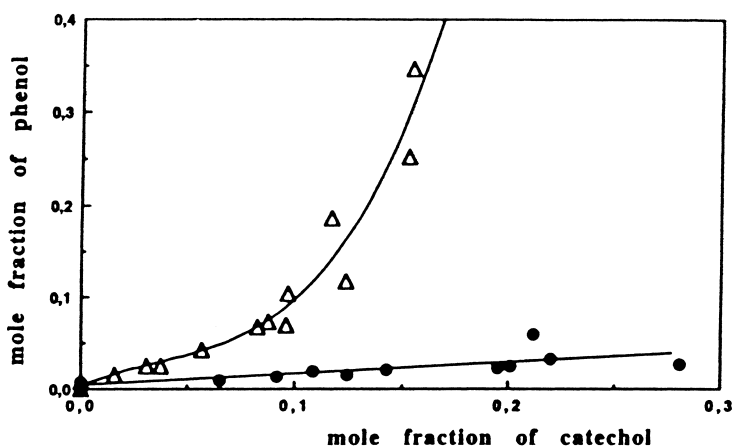


Fig. 22. Product distribution from HDO of guaiacol (●), catechol (Δ), phenol (○) and their sum (★) vs. reaction time [83].

However, Laurent and Delmon [90,91] showed that, for the carbon-supported CoMo catalyst, the phenol/CAT ratio was seven times greater than that for the  $\text{Al}_2\text{O}_3$ -supported catalyst (Fig. 23). This observation

was attributed to a direct elimination of the methoxy group via hydrogenolysis of the  $\text{C}_{\text{AR}}-\text{O}$  bond. Thus, carbon support is considered an inert material. A similar network was proposed by Petrocelli and Klein [81] during their study on the HDO of methyl-GUA, eugenol and vanillin. The product distribution from the HDO of 4-propylGUA over  $\text{Mo}/\text{Al}_2\text{O}_3$  differed significantly from that over  $\text{NiMo}/\text{P}\cdot\text{Al}_2\text{O}_3$  [94]. The catalyst with the acidic support promoted dealkylation to *m*- and *p*-methylphenols, ethyl- and methylpropylphenols, whereas for the  $\text{Mo}/\text{Al}_2\text{O}_3$  catalyst, *p*-propylphenol was the main product. Vuori et al. [95] reported a beneficial effect of catalyst sulphidation and the presence of sulphur in the feed on the GUA conversion. The product distribution was also influenced by sulphur. Thus, the formation of veratrole, anisole (ANI) and methylCAT was observed in addition to CAT and phenol. Kallury et al. [92] compared the reactivity of CAT with that of the *m*- and *p*-dihydroxybenzenes. The *m*- and

Fig. 23. Yield of phenol as a function of yield of catechol, CoMo on  $\text{Al}_2\text{O}_3$  (●) and carbon (Δ) [84].

*p*-dihydroxybenzenes gave primarily products of ring saturation, whereas the CAT was converted mostly to phenol. Tropinen and Bredenberg [89] studied methoxythiophenols in the presence of a sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst at 528 K and an H<sub>2</sub> pressure of 5.0 MPa. They observed a 97.4% HDS conversion and only 2.5% HDO conversion to hydrocarbons.

Laurent and Delmon [83,90] used 4-methylacetophenone (4MA) and diethylsebacate (DES) to study the HDO of ketones and esters. The reaction network proposed by these authors is shown in Fig. 24 [90]. De-esterification also occurred presumably on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. It is noted that, for all these reactants, coke formation was much smaller than that for GUA [84]. The carbonyl group of the 4MA could be readily hydrogenated to a methylene group at 473 K over sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts, i.e., yielding 4-methyl ethylbenzene as the main product. The decarboxylation and HYD of the carboxylic group to a methyl group occurred simultaneously. It is noted that a temperature of at least 573 K was required for the latter. However, carboxylated products were predominant. At 553 K, the HDO of decanoic acid (DEC) and ethyldecanoate (EDEC) gave mainly nonane and decane with selectivity ratios nonane/decane of 1.5 and 1.1, respectively. Eskay et al. [93] observed that, at 673 K and in the absence of catalyst, only about 35% of 1,2-(4,4'-dicarboxyphenyl)ethane in tetraline was converted via decarboxylation. As observed by Afonso et al. [26], at 673 K and an H<sub>2</sub> pressure of 12.5 MPa, the conversion of carboxylic groups to methyl groups was predominant compared to decarboxylation.

## 5. Kinetics of HDO

HDO kinetics have been investigated using single-component systems and mixtures alone or in the presence of S- and N-containing compounds as well as H<sub>2</sub>S, H<sub>2</sub>O and NH<sub>3</sub>. Differences between the kinetic parameters obtained by different authors require a close examination of the experimental conditions used. In this regard, the type and form of the catalyst, test parameters, type of reactors (e.g., batch versus continuous), method of analysis, reactant concentration, type of solvent etc. may be contributors. Viljava and Krause [96], while studying the HDO of phenol, pointed out how the mass balance inaccuracies can affect kinetic parameters in batch systems. Also, LaVopa and Satterfield [97], while studying the HDO of DBF, emphasized the importance of solvent volatility compared to that of the reactant for kinetic measurements in trickle bed systems. Reliable kinetic data can contribute to the understanding of the HDO mechanism.

### 5.1. Furans

The kinetics of the HDO of single-ring compounds received little attention. Thus, only one study on the kinetics of the HDO of THF could be found [48]. This work was performed in a continuous system using a sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, near atmospheric pressure and between 533 and 573 K. On account of the H<sub>2</sub> pressure used, the study has limited applications to the conditions which are applied during hydroprocessing.

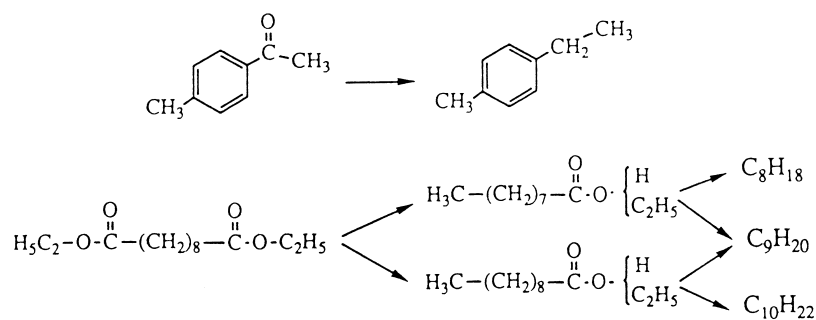


Fig. 24. Mechanism of HDO of ANI and DES [90].

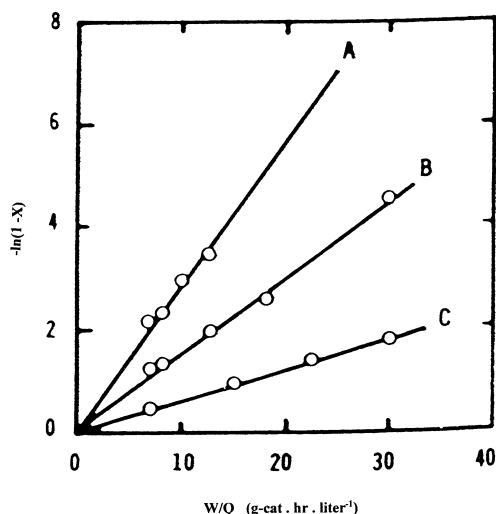


Fig. 25. Plot of  $-\ln(1-X)$  vs.  $W/Q$  for HDO of BF: (A) 340°C; (B) 325°C; (C) 310°C ( $C_R^0=0.15$  M) [50].

A Langmuir–Hinshelwood model was used in the first kinetic study on the HDO of BF carried out by Lee and Ollis [50] over a sulphided  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst below 623 K and an  $\text{H}_2$  pressure of 6.9 MPa. A competitive adsorption of reactant, oxygenated intermediates, water and trace mercaptan on one site and that of hydrogen on the other site was assumed. For a constant  $\text{H}_2$  pressure and complete conversion of mercaptan, the following first-order equation was obtained:

$$-\ln(1 - X_{\text{HDO}}) = kC_R^0 \left(\frac{w}{F}\right) = k \left(\frac{w}{Q}\right)$$

where  $X_{\text{HDO}}$  is the conversion of BF to the deoxygenated products,  $C_R^0$  is the initial reactant concentration,  $w$  is the weight of the catalyst and  $F$  is the flow rate. Similarly, the following equation was derived for HYD of BF to 2,3-dihydroBF and *o*-ethylphenol:

$$-\ln(1 - X_{\text{H}}) = k' \left(\frac{w}{F}\right)$$

where  $X_{\text{H}}$  is the BF conversion to the hydrogenated product. Below 533 K, only 2,3-dihydroBF and *o*-ethylphenol were detected. Appreciable amounts of deoxygenated products were detected above 583 K. The apparent first-order plot for the HDO of BF is shown in Fig. 25. Similar treatment of the HDO of *o*-ethylphenol in the absence of BF resulted in a large

HDO conversion at much lower temperatures than that of BF, i.e., BF almost completely inhibited the HDO of *o*-ethylphenol below 573 K. The presence of the inhibition is supported by the apparent activation energies for HDO of BF and *o*-ethylphenol estimated by Lee and Ollis [50], i.e., 138 and 71 kJ/mol, respectively.

Another kinetic study on the HDO of BF was conducted by Edelman et al. [36] over a sulphided  $\text{NiMo}/\text{Al}_2\text{O}_3$  catalyst. The kinetic analysis used by these authors was based on a similar reaction network (Fig. 6) as that used by Lee and Ollis [50]. Also, for HYD of BF, Edelman et al. [36] assumed a competitive adsorption of reactant, oxygenated intermediates, water and mercaptan on one site. Other assumptions included a similarity of the equilibrium adsorption constants for reactant, oxygenated intermediates and water. Further, it was assumed that, when HYD of BF predominates, the concentration of water is negligible. The following form of the Langmuir–Hinshelwood kinetic adsorption model was obtained based on the assumption that HYD is first-order in BF and is the rate-controlling step:

$$r_{\text{hyd}} = \frac{k''_{\text{hyd}} P_{\text{R}}}{1 + K_{\text{R}} P_{\text{R}} + K_{\text{s}} P_{\text{s}} + K_{\text{w}} P_{\text{w}} + \sum_i K_{\text{pi}} P_{\text{pi}}}$$

where  $P_{\text{R}}$ ,  $P_{\text{s}}$ ,  $P_{\text{w}}$  and  $P_{\text{pi}}$  are partial pressures of the reactant, mercaptan in the feed, water and oxygenated intermediates, respectively, and  $K_{\text{R}}$ ,  $K_{\text{s}}$ ,  $K_{\text{w}}$  and  $K_{\text{pi}}$  are the corresponding adsorption constants. Combining this equation with the mass conservation equation for BF, as well as some rearrangements and integration, the following relationship was obtained:

$$-\ln \left( \frac{P_{\text{R}}}{P_{\text{R},0}} \right) = k_{\text{hyd}} \left( \frac{W}{F} \right)$$

where  $P_{\text{R},0} = P_{\text{R}} + P_{\text{w}} + P_1 + P_2 + P_3$ , i.e., the sum of partial pressure of BF and oxygenated intermediates (Fig. 6),  $k_{\text{hyd}}$  is the HYD rate constant,  $F$  is the inlet molar flow rate of BF and  $W$  is the weight of catalyst in the packed bed. An essentially linear correlation between  $\ln(P_{\text{R}}/P_{\text{R},0})$  and  $W/F$  was obtained. An analogous equation for HDO would have the following form:

$$-\ln \left( \frac{P_{\text{ox}}}{P_{\text{R},0}} \right) = k_{\text{HDO}} \left( \frac{W}{F} \right)$$

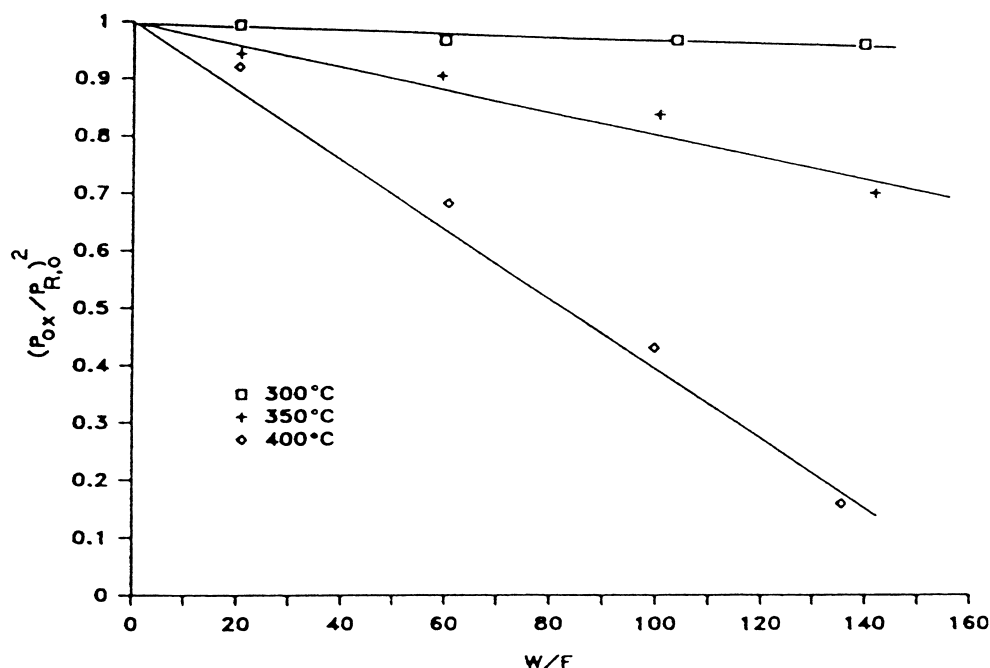


Fig. 26. Plot of  $(P_{\text{ox}}/P_{\text{R,O}})^2$  vs.  $W/F$  for HDO of BF [36].

where  $P_{\text{ox}} = P_{\text{R}} + P_1 + P_2 + P_3$ . Experimental data in the form  $-\ln(P_{\text{ox}}/P_{\text{R,O}})$  versus  $W/F$  showed that the observed HDO does not follow first-order kinetics above 623 K and high space times. Thus, an increase in  $k_{\text{hdo}}$  with decreasing  $P_{\text{ox}}$  suggests a self-inhibiting effect of the oxygenated compounds. A zero-order model examined by Edelman et al. [36] was also rejected. Subsequently, these authors examined the following model:

$$\frac{-d(P_{\text{ox}}/P_{\text{R,O}})}{d(W/F)} = \frac{k(P_{\text{ox}}/P_{\text{R,O}})}{\{1 + K(P_{\text{ox}}/P_{\text{R,O}})\}^2}$$

After a simplification, this equation was integrated to yield

$$\left(\frac{P_{\text{ox}}}{P_{\text{R,O}}}\right)^2 = 1 - 2k_{\text{hdo}}\left(\frac{W}{F}\right)$$

A plot of  $(P_{\text{ox}}/P_{\text{R,O}})^2$  versus  $W/F$ , shown in Fig. 26, appears linear for the  $(-1)$ -order model. An apparent HDO activation energy estimated from these values was 106 kJ/mol.

The rate constants estimated by Edelman et al. [36] and Lee and Ollis [50] are compared in Table 6. Dif-

ference between the experimental conditions of these studies is emphasized. First of all, the reactant concentration of the former was much higher than that used by Lee and Ollis [50], indicating a more extensive self-inhibition by the reactant. Also, the ratio of BF to sulphur agent was about 20 times greater in the study conducted by Edelman et al. [36]. Then,  $\text{H}_2\text{S}$  in excess of that required to maintain catalyst in a sulphided form inhibited the HDO reactions [48].

Table 6  
Rate constants for hydrogenation and HDO of BF

Temperature (K)	$k_{\text{hyd}} \times 10^7$ (l/s g cat)	$k_{\text{hdo}} \times 10^7$ (l/s g cat)
Edelman et al. [36] <sup>a</sup>		
573	10.2	0.5
623	28.8	5.0
673	46.7	14.0
Lee and Ollis [50] <sup>b</sup>		
573	–	3.0
598	–	6.5

<sup>a</sup>  $k_{\text{hyd}}$ : pseudo-first-order;  $k_{\text{hdo}}$ :  $(-1)$ -order; concentration of BF: 0.6 mol/l; NiMo/Al<sub>2</sub>O<sub>3</sub>; 0.3 mol of dimethyl sulphide.

<sup>b</sup>  $k_{\text{hdo}}$ : pseudo-first-order; concentration of BF: 0.15 mol/l; CoMo/Al<sub>2</sub>O<sub>3</sub>; 0.0075 mol of mercaptan.

The detailed evaluation of the HDO kinetics of DBF was conducted by Krishnamurthy et al. [57]. They used differential equations for an isothermal batch reactor, assuming  $H_2$  to be in excess. These equations were integrated with respect to the time for various time intervals. The rate constants were determined by minimizing the sum of squares of a weighted error using the integrated solution. The effects of  $H_2$  pressure, temperature and initial DBF concentration on the rate constants were determined. The rate constants estimated by these authors for several steps occurring during the HDO of DBF show that conversion to single-ring products was the fastest step. The kinetic study of LaVopa and Satterfield [59], conducted in a continuous system, confirmed the formation of single-ring products as the main route during the HDO of DBF as well. This involved formation of oxygenated intermediates which were rapidly converted to single-ring products. In the presence of the sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, the reaction was first-order in  $H_2$  and DBF; however, for the oxidic catalyst, the reaction was zero-order with respect to DBF. These authors used the least-square regression to fit first-order rate constants to the data. The rate equation was of the following form:

$$\frac{d(1-x)}{dt} = -k(1-x)$$

where  $x$  is the DBF conversion,  $k$  the first-order rate constant (mol/h g cat),  $t$  the space time (h g cat/mol DBF). The effect of temperature on the rate constants determined in this study is shown in Fig. 27. The activation energy estimated from these results was 67 kJ/mol compared to 68.4 and 76.2 kJ/mol estimated by Krishnamurthy et al. [57] for the conversion of DBF to biphenyl and cyclohexylbenzene, respectively. Girgis and Gates [75] determined the rate constants for the simplified network shown in Fig. 28. They also confirmed the formation of single-ring products as the main route during the HDO of DBF. The rate constants obtained by these authors are compared with those obtained by LaVopa and Satterfield [59] in Table 7. A significantly greater reactant concentration used by these authors may be at least partly responsible for the difference. Also, in their study, the presence of  $H_2S$  inhibited HDO reactions as was indicated by a rapid increase in the HDO conversion after  $H_2S$  removal from the system. As expected, the HDO

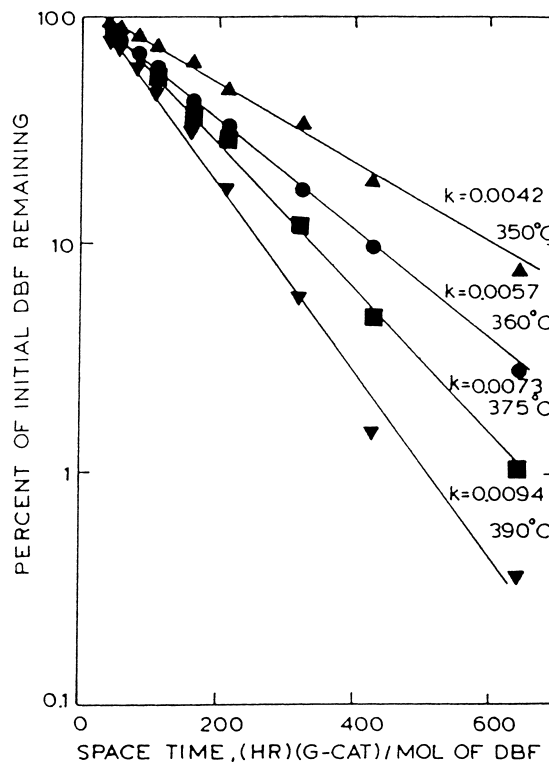


Fig. 27. Effect of temperature on rate constant for HDO of DBF [59].

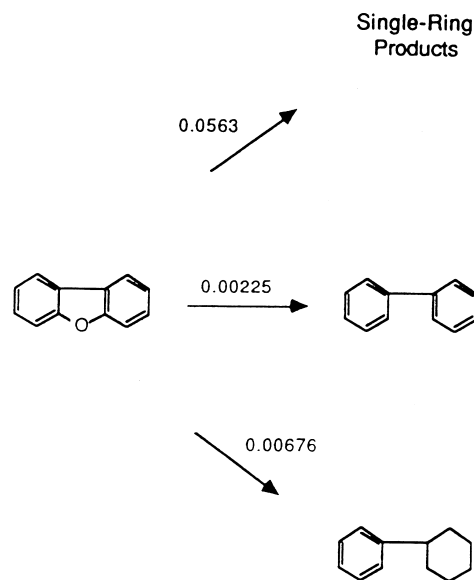


Fig. 28. Simplified mechanism for HDO of DBF [75].

Table 7  
Rate constants for HDO of DBF

Temperature (K)	$k_{\text{hdo}} \times 10^6$
LaVopa and Satterfield [59] <sup>a</sup>	
623	4.8
633	6.5
648	8.3
663	10.7
Girgis and Gates [75] <sup>b</sup>	
623	18.1

<sup>a</sup> 7 MPa; 0.245 mol/l; 13.9 kPa H<sub>2</sub>S.

<sup>b</sup> 17 MPa; 0.0004 mol/l; 0.0001 mol/l 3,7-dimethylDBT.

of DBF was poisoned by NH<sub>3</sub> [98] and quinoline [47].

The difference in experimental conditions used in various HDO studies prevents direct comparison of the rate constants. To overcome this problem, Girgis and Gates [75] expressed rate constants relative to that of the most rapid reaction in the overall HDO mechanism of DBF to compare their results with those obtained by Krishnamurthy et al. [57]. The results in Table 8 show a good agreement between the two studies. The comparison became a challenge when kinetic data was obtained for a single compound in a mixture with other heterocyclics and aromatics. Gates et al. [7,60,99] studied the HDO of DBF in the mixture containing pyrene, phenanthrene, fluoranthene and DBT with and without 5,6,7,8-tetrahydro-1-naphthol as well as that in a neutral oil fraction which was isolated from a CDL. The obtained pseudo-first-order rate constants are compared in Table 9 together with that obtained for a single DBF [75].

## 5.2. Phenols

Kinetic studies on the HDO of single phenols or mixtures of phenols were conducted in a trickle bed re-

Table 8  
Relative values of the pseudo-first-order rate constants

Reaction	Reference	
	[75]	[57]
DBF⇒single-ring compounds	1.0	1.0
DBF⇒cyclohexylbenzene	0.11	0.07
DBF⇒biphenyl	0.04	0.03

Table 9  
Pseudo-first-order rate constants for HDO of DBF (l/g cats×10<sup>6</sup>) [75]

Single compound	
Single-ring products	16.0
Biphenyl	0.6
Phenylcyclohexyl	1.9
In mixture A (single-ring products)	
with 5,6,7,8-tetrahydronaphthol	5.8
without 5,6,7,8-tetrahydronaphthol	13.0
In neutral oil	
DBF disappearance	7.4

actor [18,21,50,51,60,62–64,80] and in a batch reactor [68,71,73,100]. Sulphided commercial CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts were the most frequently used catalysts.

The batch reactor study conducted by Gevert et al. [68] focussed on the HDO of 2-, 4- and 2,6-substituted phenols. The simplified reaction network used is shown in Fig. 29. The following equations to relate mole fractions of the phenols ( $X_A$ ), aromatics ( $X_B$ ) and cyclohexane+cyclohexene ( $X_C$ ), with the pseudo-first-order rate constants, were derived:

$$X_B = \frac{k_1}{k_1 + k_2} (1 - X_A)$$

and

$$X_C = \frac{k_2}{k_1} X_B$$

The pseudo-first-order rate constants were calculated from the following equation:

$$\frac{dX_B}{df(t/V)} = k_1 W X_A$$

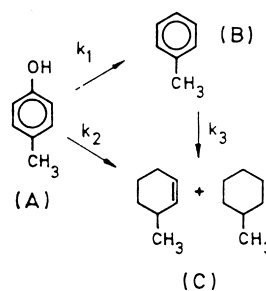


Fig. 29. Simplified mechanism for HDO of 4-methylphenol [68].

Table 10  
Pseudo-first-order rate constants for HDO methyl phenols over sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> at 573 K

Phenol+Poison	$k_1$ (l/g cat s × 10 <sup>5</sup> )	$k_2$ (l/g cat s × 10 <sup>5</sup> )
Ref. [68]		
4-MP	4.0	0.9
4-MP <sup>a</sup>	6.5	1.3
2-MP	2.1	0.3
2,4-diMP	2.5	0.3
2,6-diMP	0.5	0.2
2,4,6-triMP	0.8	0.1
4-MP+NH <sub>3</sub> (8.5) <sup>b</sup>	0.8	0.1
4-MP+NH <sub>3</sub> (43)	0.2	0.03
4-MP+H <sub>2</sub> S (36)	0.5	0.8
4-MP+H <sub>2</sub> S (72)	0.2	0.6
Ref. [79]		
Phenol <sup>c</sup>	1.1	
(Ref. [50]; continuous system)		
2-EtP <sup>c</sup>	1.1	
3-MP	1.6	

<sup>a</sup> Initial concentration 70 mmol/l, all other runs 142 mmol/l.

<sup>b</sup> Numbers in brackets indicate concentration of poison in mmol/l.

<sup>c</sup> Extrapolated from Arrhenius plots.

The initial slope of the curve for conversion versus  $f(t/V)$  allowed calculation of  $k_1$ . In this equation,  $V$  is the volume of the feed at time  $t$ . The  $k_2$  could then be obtained in conjunction with the above equations. The obtained rate constants are summarized in Table 10 including constants obtained in the presence of NH<sub>3</sub> and H<sub>2</sub>S. The poisoning effect on the overall HDO is quite evident. The rate constants increased with decreasing concentration of substrate, indicating a self-inhibiting effect of the latter on its HDO. In the subsequent study, Gevert et al. [100] conducted a detailed comparison of the 3,5- and 2,6-dimethyl phenols. For the former,  $k_1$  was about 10 times greater than that for 2,6-dimethylphenol, whereas for  $k_2$ , the difference was much less evident. The Arrhenius plots in Fig. 30 show that the activation energies for hydrogenolysis were greater than for the HYD of ring. For 2,6-dimethylphenol, HYD increased relative to hydrogenolysis with increasing temperature, whereas an opposite trend was observed for the 3,5-dimethylphenol.

Laurent and Delmon [71] conducted a detailed study on the effect of *o*-ethylphenol, NH<sub>3</sub>, H<sub>2</sub>S and H<sub>2</sub>O on the HDO of *p*-methylphenol in a batch

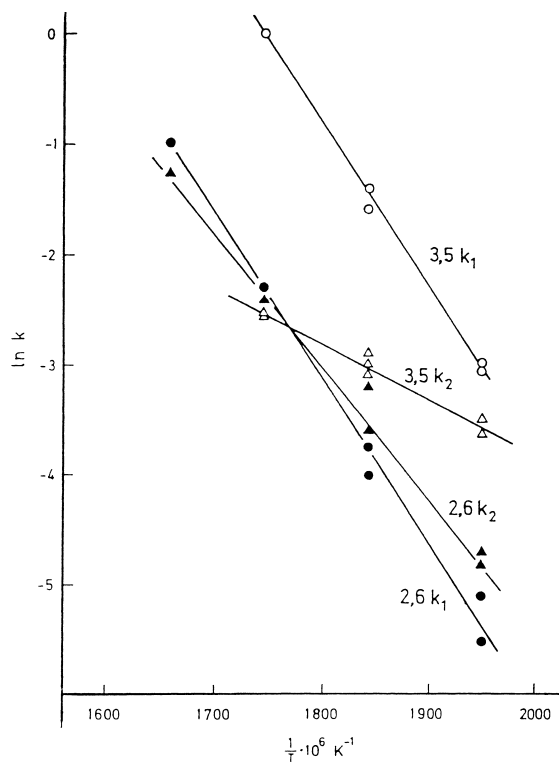


Fig. 30. Arrhenius plots for  $k_1$  (○),  $k_2$  (△), 3,5-dimethylphenol (○, △) and 2,6-dimethylphenol (●, ▲) [100].

reactor system. The single compound experiments showed that *p*-methylphenol was much more reactive than *o*-ethylphenol, i.e., less than 13% of the former's conversion. The HDO of *p*-methylphenol was inhibited by *o*-ethylphenol. As expected, NH<sub>3</sub> severely poisoned the HDO reactions, whereas H<sub>2</sub>O had little effect. H<sub>2</sub>S had a much more pronounced effect on the hydrogenolysis reactions than on the HYD reactions. The effect of these agents on HDO over a CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst differed from that over a NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst (Table 11), e.g., for the latter, the  $k_{MCH}/k_{TOL}$  was significantly greater than that for the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. Laurent and Delmon [101] expanded their study to include high H<sub>2</sub>O pressure conditions with the aim of simulating the HDO occurring during high pressure liquefaction of biomass. Thus, the H<sub>2</sub>O and H<sub>2</sub>S vapor pressure was 2.5 and 0.1 MPa, respectively, of the total pressure of 7 MPa. It should be noted that the H<sub>2</sub>O saturation pressure under the conditions used by these authors

Table 11  
Pseudo-first-order rate constants for HDO of 4-methylphenol in the presence of *o*-ethylphenol, H<sub>2</sub>O, NH<sub>3</sub> and H<sub>2</sub>S [71]<sup>a</sup>

Agent	Rate constant × 10 <sup>5</sup>			
	CoMo		NiMo	
	<i>k</i> <sub>MCH</sub>	<i>k</i> <sub>TOL</sub>	<i>k</i> <sub>MCH</sub>	<i>k</i> <sub>TOL</sub>
<i>o</i> -Ethylphenol (mol/l)				
0	2.5	2.9	13.6	0.7
0.145	1.3	1.2	7.2	0.4
0.434	0.8	0.7	3.6	0.2
H <sub>2</sub> O (mol/l)				
0	0.9	1.0	4.2	0.2
0.65	1.1	0.8	4.3	0.2
1.96	1.1	0.7	3.2	0.2
NH <sub>3</sub> (mmol/l)				
0	1.9	2.0	6.2	0.6
5	1.6	1.4	4.3	0.3
9	1.3	1.0	3.2	0.2
49	0.6	0.3	1.1	0.1
H <sub>2</sub> S (mmol/l)				
0	0.7	3.7	5.3	0.5
17	0.8	2.0	5.3	0.3
49	0.9	1.0	4.2	0.2
98	1.0	0.7	3.9	0.2
H <sub>2</sub> O (25 bar)			0.85	0.05
H <sub>2</sub> O+H <sub>2</sub> S (25 bar+1.1 bar)			1.37	0.06

<sup>a</sup> Conditions: batch stirred reactor, 613 K, 7 MPa of H<sub>2</sub>, dodecane solvent; 0.327 mol/l.

was 17 MPa. Table 11 indicates the poisoning effect of H<sub>2</sub>O and a protective effect of H<sub>2</sub>S.

Cho and Allen [79] used a batch reactor system to study the HDO kinetics of chlorophenols and phenol over a sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst under similar conditions as those used by Gevert et al. [68]. The rate constants for the dechlorination were more than two orders of magnitude greater than those for HDO, suggesting that dechlorinated phenol played a key role during the overall HDO of the chlorophenols. At the same time, these authors estimated rate constants for the HDO of the phenol. The pseudo-first-order rate constant in Table 10 is the value which was extrapolated from the constants estimated at lower temperatures. Surprisingly, the kinetics of the phenol attracted much less attention than that of the substituted phenols.

Odebunmi and Ollis [63] studied the HDO of cresols in a trickle bed reactor over a sulphided CoMo/Al<sub>2</sub>O<sub>3</sub>

catalyst. They observed approximately first-order dependence on H<sub>2</sub> pressure and pseudo-first-order behavior of the HDO conversion of cresols at a constant H<sub>2</sub> pressure. The rate constants were determined from the plots, such as ln(1-*X*<sub>C</sub>) versus *P*<sub>H<sub>2</sub></sub> and ln(1-*X*<sub>C</sub>) versus *W/F*, respectively, where *X*<sub>C</sub> is the cresol conversion and the others are the commonly known parameters. The rate constants estimated by these authors were about two orders of magnitude smaller than those estimated by Gevert et al. [68] and Laurent and Delmon [71]. Apparently, the catalyst in the study of Odebunmi and Ollis [61] was already deactivated before the measurements were taken in addition to different experimental systems used. In subsequent studies, these authors estimated the pseudo-first-order rate constant at 573 K for the HDO of *m*-cresols [64] and *o*-ethylphenol [50] to be in the range of those shown in Tables 10 and 11, i.e., 1.6 × 10<sup>-5</sup> and 1.1 × 10<sup>-5</sup> l/g cat s, respectively. Temperature can influence relative reactivities of cresols. This is supported by the results in Fig. 31 [62] which show that, for *o*- and *p*-cresols, the differ-

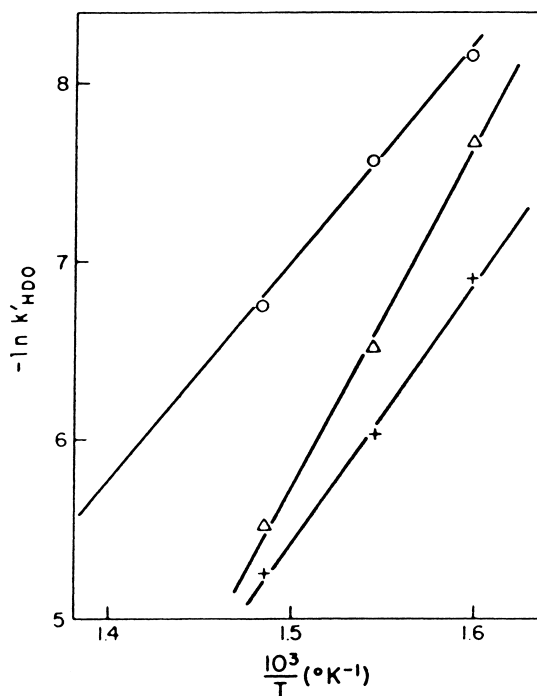


Fig. 31. Arrhenius plots for (○) *o*-cresol, (Δ) *p*-cresol and (+) *m*-cresol [62].



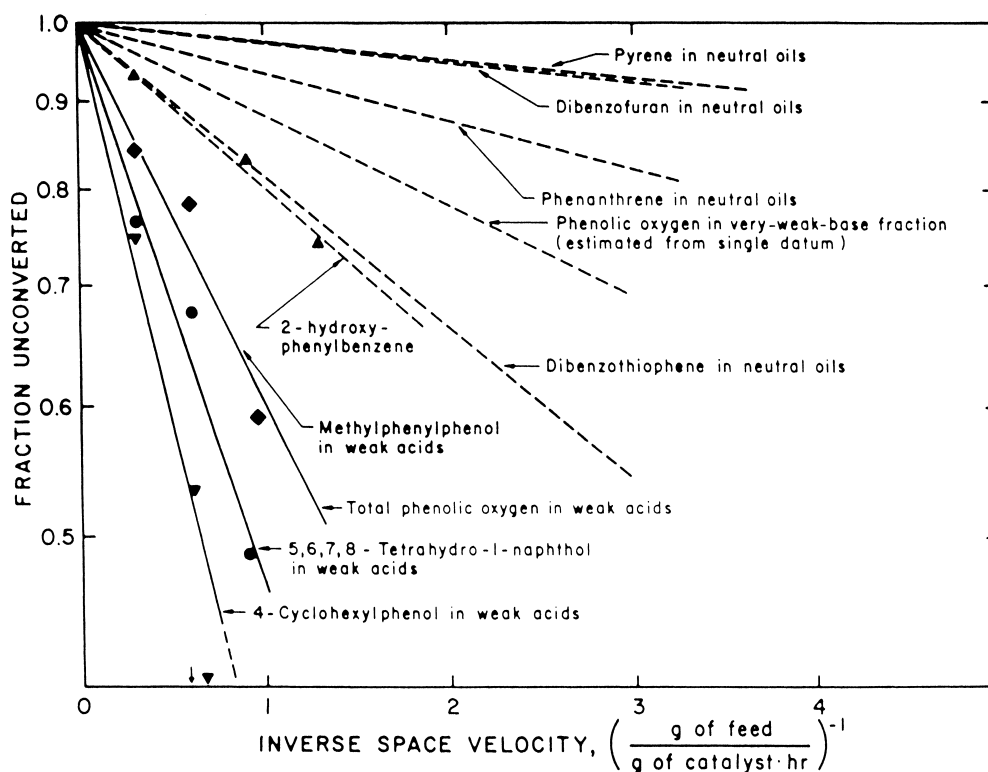


Fig. 32. Effect of inverse space velocity on HDO conversion of model compounds [20].

ence in reactivity decreases with increasing temperature. Activation energies for the HDO of *o*-, *m*- and *p*-cresols estimated from these results were 96, 113 and 156 kJ/mol, respectively, compared to 125 kJ/mol for the phenol estimated in a batch reactor [79].

Gates et al. [7,20,21] conducted studies on the HDO of phenols in mixtures isolated from a CDL over a sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The very weak acid and weak acid fractions contained only low concentrations of sulphur and nitrogen and high concentrations of the O-containing compounds, i.e., 8.90 and 9.79 wt.%, respectively [16]. These fractions were used as 0.25 wt.% solutions in cyclohexane. In one study, the product analysis was performed using IR and GC-MS techniques [21], whereas in the other study, the GC-MS technique was used to identify compounds and FID chromatography to determine their concentrations [20]. The results in Fig. 32 and Table 12 show that the method of analysis influences the values. Comparison of the rate constants for pure 2-hydroxyphenylbenzene and that in the mixture in-

dicates inhibition of HDO by other compounds. The rate constants in Table 12 were obtained at 623 K, compared to those in Tables 10 and 11 which were obtained at 573 K. Besides the different experimen-

Table 12  
Pseudo-first-order rate constants for disappearance in mixtures (l/g cat s × 10<sup>4</sup>)<sup>a</sup>

	[21]	[20]
Pure compound in cyclohexane		
2-Hydroxyphenylbenzene	1.5	
Weak acid fraction in cyclohexane		
2-Hydroxyphenylbenzene	0.83	1.8
Methylphenylphenol	1.52	2.0
4-Cyclohexylphenol	4.46	6.2
5,6,7,8-Tetrahydro-1-naphthol	1.91	4.2
Methyltetrahydronaphthol	–	4.5
Dimethyldihydroxyindan	–	4.6
1-Naphthol	–	5.4
Phenolics in weak acids	1.56	

<sup>a</sup> Conditions: flow reactor; sulphided NiMo/Al<sub>2</sub>O<sub>3</sub>; cyclohexane solvent; 623 K; 12 MPa.

Table 13  
Activation energies of reactions in Fig. 18 [73]

Reaction	Activation energy (kJ/mol)
1	139±32
2	100±23
3	44±20
4	132±38
5	77±23

tal systems used, i.e., batch versus continuous, other parameters may be responsible for the difference in values. Of particular importance is the concentration of reactant, which in the case of the Gevert et al. [68] and Laurent and Delmon [101], was more than an order of magnitude greater than that used by Gates et al. [7,20,21], indicating a much lower degree of self-inhibition. A higher H<sub>2</sub> pressure used by the latter authors may also contribute to the difference.

Kinetics of the HDO of naphthol were investigated by Li et al. [73] over a sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The pseudo-first-order rate constants estimated at 427 K for all steps are shown in Fig. 18. It is evident that, at this temperature, direct HDO of naphthol is slower than ring HYD. However, above 550 K, direct HDO exceeded HYD. This is supported by the activation energies shown in Table 13. The pseudo-first-order rate constants for the disappearance of the naphthol and 5,6,7,8-tetrahydro-1-naphthol shown in Table 12 were estimated for a diluted acidic fraction derived from a CDL. Based on this data, it is suggested that the HDO reactivity of naphthol is similar to that of *m*- and *p*-substituted phenols.

### 5.3. Ethers

The pseudo-first-order rate constants (l/s g cat) for the disappearance of ANI, estimated by Hurff and Klein [102] over a sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst at 523, 548 and 598 K, were  $0.0763 \times 10^{-3}$ ,  $0.603 \times 10^{-3}$  and  $2.78 \times 10^{-3}$ , respectively. However, phenol was the major product. Then, the HDO of phenol will govern the overall HDO of ANI. In this temperature range, a value for the activation energy of 124 kJ/mol was obtained. Dibenzylether and benzodioxan (sulphided NiMo/Al<sub>2</sub>O<sub>3</sub>, 648 K and 6.9 MPa) were much more reactive than *m*-ethylphenol [51]. Shabtai et al. [82] determined the pseudo-first-order rate con-

stant for hydrogenolysis of diphenylether at 623 K and about 14 MPa pressure of H<sub>2</sub> for CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts, as well as the Mo/Al<sub>2</sub>O<sub>3</sub> catalysts promoted by the group VIII metals. For the three different CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts, the rate constant varied between  $2 \times 10^{-4}$  and  $4 \times 10^{-4}$  l/g cat s, whereas that for an NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst was about  $1 \times 10^{-4}$  l/g cat s. Apparently, in this study [82], phenol was the primary product but was rapidly converted to hydrocarbons. Thus, the rate constants approach that for an overall HDO. Artok et al. [80] observed that, besides different product distribution (indicated above), the HDO of dinaphthylether was much faster than that of the diphenylether. They suggested that the lower resonance stability of the phenoxy radicals compared to that of the naphthoxy radicals was at least partly responsible for the lower reactivity of the diphenylether. Kirby et al. [70] compared XA with dinaphthylether and found the former to be much less reactive. However, the study was conducted in the presence of a Co–Mo organometallic precursor rather than a typical hydroprocessing catalyst.

### 5.4. Bio-oil compounds

The detailed study on the kinetics of bio-oil related model compounds was published by Laurent and Delmon [83,91]. The work was conducted in a batch reactor from 523 to 573 K and an H<sub>2</sub> pressure of 7 MPa in the presence of commercial CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts kept in a sulphided form. The conversion data was fitted to the following first-order kinetic equation:

$$-\ln X_i = kWt$$

where  $X_i$  is the ratio of the concentration of the reactant in the sample ( $C_i$ ) to the concentration of the reactant in the initial sample ( $C^0$ ),  $k$  is the pseudo first-order rate constant ( $\text{min}^{-1} \text{g cat}^{-1}$ ),  $W$  is the weight of catalyst and  $t$  is the time. Pseudo-first-order logarithmic plots for 4MA, DES and GUA are shown in Fig. 33. In most cases, the experimental data did not follow pseudo first-order over the whole conversion range, i.e., only the first points were used in the determination of the rate constants. Deviation from the first-order kinetics occurred at high conversions. Fast and slow conversion ranges were observed for GUA.

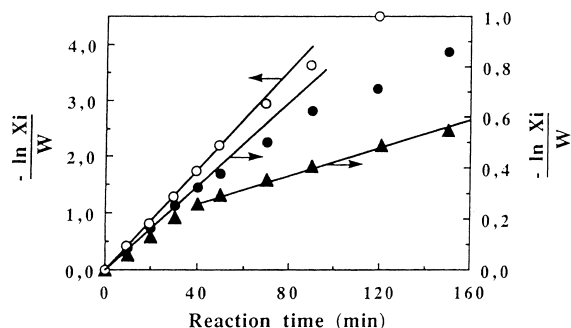


Fig. 33. Typical pseudo-first-order plot for conversion of 4MA (●) (DES ○) and (GUA ▲) [90].

This resulted from a rapid coke deposition during the early stages of the experiments. It was established that reactants with two O-containing substituents in the benzene ring form coke with greater ease than those with one O-containing substituent [84,102]. The experiments were performed for pure compounds in the presence and the absence of H<sub>2</sub>O, H<sub>2</sub>S and NH<sub>3</sub>. The results obtained by these authors at 553 K are shown in Table 14. The reactivity of 4MA is significantly greater than that of DES and GUA, suggesting a high reactivity of ketones under hydroprocessing conditions. This agrees with the results on the HDO of

Table 14

Pseudo-first-order rate constants for the HDO of 4-methylacetophenone (4MA), di-ethyldecanedioate (DES) and guaiacol (GUA)<sup>a</sup>

	Rate constant (min <sup>-1</sup> g cat <sup>-1</sup> × 10 <sup>3</sup> )		
	<i>k</i> <sub>4MA</sub>	<i>k</i> <sub>DES</sub>	<i>k</i> <sub>GUA</sub>
<b>NiMo</b>			
Reactant (R)	54.8	7.6	4.2
R+0.85 mol/l H <sub>2</sub> O	50.1	6.3	4.0
R+16 mmol/l NH <sub>3</sub>	47.7	1.8	3.2
R+96 mmol/l NH <sub>3</sub>	59.0	1.0	1.3
R+49 mmol/l H <sub>2</sub> S	54.8	7.6	4.2
R+98 mmol/l H <sub>2</sub> S	45.7	8.9	4.8
<b>CoMo</b>			
Reactant (R)	57.8	6.1	3.3
R+0.85 mol/l H <sub>2</sub> O	51.0	5.2	3.2
R+14 mmol/l NH <sub>3</sub>	52.3	2.2	2.2
R+95 mmol/l NH <sub>3</sub>	46.1	1.5	1.5
R+49 mmol/l H <sub>2</sub> S	57.8	6.1	3.3
R+98 mmol/l H <sub>2</sub> S	58.1	6.8	3.7

<sup>a</sup> T=553 K, 7 MPa, 25 mmol/l of CS<sub>2</sub> [90].

anthrone published by Kirby et al. [70], who observed O removal even under non-catalytic conditions. The values of *k*<sub>4MA</sub> in Table 14 are in good agreement with those determined by Durand et al. [103] for six ketones including benzophenone. In addition, the rate constants for HDO of adamantanol and diphenyl methanol, determined by these authors, were an order of magnitude greater than those for the HDO of ketones. The high reactivity of the ketone group may be the reason for the little poisoning observed in the presence of NH<sub>3</sub> during HDO of 4MA, compared to the severe poisoning of the HDO of DES and GUA. The values of *k*<sub>DES</sub> and *k*<sub>GUA</sub> (Table 14) indicate a higher activity of the NiMo/Al<sub>2</sub>O<sub>3</sub> compared to the CoMo/Al<sub>2</sub>O<sub>3</sub>; however, the differences are small. The rate constants in Table 14 are for the disappearance of the reactants. Thus, only 4MA was completely converted to hydrocarbons, whereas the DES and GUA products still included O-containing species. Evaluation of ethyl EDEC and DEC under the same conditions revealed that their conversion to hydrocarbons was greater than that of DES. This suggests that the hydrogen consumption and/or its availability influences the overall HDO reaction. Delmon et al. [91] expanded their work to include unsupported CoMoS and that supported on γ-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and carbon, as well as γ-Al<sub>2</sub>O<sub>3</sub> alone. The pseudo-first-order rate constants for the reactant disappearance in Table 15 were obtained at 553 K and 7 MPa of H<sub>2</sub>. These results, together with those shown in Table 16, suggest that the structure of catalysts and their acidity have an effect on both the mechanism and the kinetics, as is evidenced by the difference in decarboxylation of DES and the phenol/CAT ratio from the GUA reaction. The γ-Al<sub>2</sub>O<sub>3</sub> support exhibited some activity as well. Other aspects of the effect of the catalyst structure will be discussed later in the review.

Using a batch reactor system, Hurff and Klein [102] compared the kinetics of the disappearance of GUA and ANI over a sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst between 523 and 623 K and 3.5 MPa of H<sub>2</sub>. The reactant concentration (in hexadecane) was about 0.03 mol/l. The pseudo-first-order rate constant for GUA disappearance was about 30 times greater than that for ANI, suggesting that the electronic enhancement of the *ortho*-hydroxy substituent is more significant than any steric hindrance it may cause. However, Bredenberg et al. [86], while studying the same reactants

Table 15

Pseudo-first-order rate constants for disappearance of 4-MA, DES and GUA and % DES decarboxylation and GUA phenol/CAT and coke on catalyst after reaction [91]

Catalyst	Rate constant (cm <sup>3</sup> /min g cat)					Coke (wt.%)
	<i>k</i> <sub>4MA</sub>	<i>k</i> <sub>DES</sub>	% Decarboxylation	<i>k</i> <sub>GUA</sub>	Phenol/CAT	
γ-Al <sub>2</sub> O <sub>3</sub>	0.15	0.32	nil	0.35	~0	10.4
CoMo/Al <sub>2</sub> O <sub>3</sub>	9.69	0.70	36	1.30	12.6	9.0
CoMo/SiO <sub>2</sub>	1.97	0.17	nil	0.28	2.0	2.7
CoMoC	7.79	0.83	22	0.22	89.3	–
CoMoS	0.82	0.77	nil	0.39	8.0	2.9

in a continuous system in the presence of a typical hydrocracking catalyst, i.e., NiMo/SiO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub>, observed ANI to be more reactive. In this case, the reactants (45 mol%) were mixed with benzene. It is assumed that, in the case of GUA, the higher acidity of the support compared to that of γ-Al<sub>2</sub>O<sub>3</sub> caused rapid catalyst deactivation. Also, a rather different presulphiding procedure was used by these authors. Nevertheless, in spite of the differences, the product distribution was similar in both studies. These two studies may be used to illustrate the effect of different experimental conditions on the final results, although with respect to HDO, they have only a limited value because only the reactant disappearance was followed, i.e., phenols were the main products.

The activation energies reported in several studies are summarized in Table 17, as well as in Table 18, for bio-oil related compounds. Differences for the same reaction from different workers are attributed to experimental conditions which varied from study to study. For example, for single-compound estimates, the same reactant concentration was not always used, indicating a different extent of self-inhibition. Also, temperature regions and the time on stream when the estimates were made varied. As the results in Table 18 show, the

latter factor is important when catalyst deactivation affects the reaction. Other parameters include H<sub>2</sub> pressure, type and form of catalyst, experimental system etc. In the case of multi-reactant systems, estimates of activation energies for HDO will be affected by HDS and HDN. Nevertheless, in some cases, an agreement among several workers is quite remarkable. Activation energies may indicate change in relative reactivities with the temperature change. For example, results obtained by Odeunmi and Ollis [62] suggest that the reactivity of *p*-cresol will increase relative to that of *o*- and *m*-cresol with increasing temperature. However, as Fig. 31 shows, in the temperature region which is typical of hydroprocessing, their relative reactivities will not change. The values estimated by Li et al. [73] represent another example of how activation energy can be used to predict the change of the overall HDO mechanism (Fig. 18) with the change of temperature.

## 6. HDO reactivities of O-containing compounds

Relative HDO reactivities of the O-containing compounds were discussed by Landau [104] and Afonso et al. [26], who pointed out complexities in establishing a true order. For the purpose of this discussion, reactivity is defined as the overall conversion of an O-compound to a hydrocarbon rather than to an O-containing intermediate. Grange et al. [105] used the iso-reactivity, i.e., the temperature at which a significant identical value of conversion (to hydrocarbons) can be attained in the presence of a commercial hydroprocessing CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The reactivity trends established from these values are shown in Table 19. They pointed out that aliphatic ethers and alcohols are even more reactive than ketones. Böhringer

Table 16

Acidity of fresh catalysts and their coke content after reaction [91]

	Acidity (μeq NH <sub>3</sub> /g)	Coke (wt.%)
γ-Al <sub>2</sub> O <sub>3</sub>	359	10.4
CoMo/Al <sub>2</sub> O <sub>3</sub>	522	9.0
CoMo/Al <sub>2</sub> O <sub>3</sub> /K	456	10.0
CoMoSiO <sub>2</sub>	113	2.7
CoMoC	111	–
CoMoS	n.d.	2.9

Table 17  
Summary of activation energies<sup>a</sup>

Reaction	Catalyst	Activation energy (kJ/mol)	Reference
BF→2,3-DihydroBF	NiMo	75	[36]
BF→2,3-DihydroBF	CoMo	79	[36]
BF→Hydrocarbons	NiMo	104	[36]
BF→Hydrocarbons	CoMo	138	[36]
BF→Hydrocarbons	CoMo	138	[50]
DBF→Hydrocarbons	NiMo	67	[59]
DBF→Biphenyl	NiMo	68	[57]
DBF→Cyclohexylbenzyl	NiMo	76	[57]
DBF→Single-ring hydrocarbons	NiMo	97	[57]
Phenol→Hydrocarbons	NiMo	126	[79]
<i>o</i> -Cresol→Hydrocarbons	CoMo	96	[62]
<i>m</i> -Cresol→Hydrocarbons	CoMo	113	[62]
<i>m</i> -Cresol→Hydrocarbons	CoMo	83	[63]
<i>m</i> -Cresol→Hydrocarbons	CoMo	121	[64]
<i>p</i> -Cresol→Hydrocarbons	CoMo	108	[64]
<i>p</i> -Cresol→Hydrocarbons	CoMo	154	[62]
2,6-Dimethylphenol→Hydrocarbons	CoMo	124	[100]
3,5-Dimethylphenol→Hydrocarbons	CoMo	122	[100]
<i>o</i> -Ethylphenol→Hydrocarbons	CoMo	71	[50]
<i>o</i> -Phenylphenol→Biphenyl	NiMo	86	[57]
<i>o</i> -Phenylphenol→Cyclohexylbenzene	NiMo	71	[57]
<i>o</i> -Cyclohexylphenol→Bicyclohexyl	NiMo	74	[57]
<i>o</i> -Cyclohexylphenol→Cyclohexylbenzene	NiMo	118	[57]
Reactions in Fig.	CoMo		[73]
1		139	
2		100	
3		44	
4		132	
5		77	
DPE→Phenol+hydrocarbons	MoS <sub>2</sub>		
DPE+DHP→Phenol+hydrocarbons		55	[80]
DPE+DEC→Phenol+hydrocarbons		42	[80]
DPE alone→Phenol+hydrocarbons		112	[80]
DPE→Phenol+hydrocarbons	CoMo	148	[81]

<sup>a</sup> DPE: diphenylether; DHP: dihydrophenanthrene; DEC: decalin.

and Schultz [106] introduced the  $T_{50\text{HC}}$  parameter, defined as the temperature at which 50% conversion to O-free products was achieved.

The overall HDO conversions and the rate constants determined during the kinetic measurements are suitable parameters for determining relative HDO reactivities. However, differences in experimental conditions prevent a direct comparison of the data obtained by different workers. The results in Tables 17 and 18 show that activation energies for the HDO of individual reactants vary, suggesting that the relative reactivities will change with temperature. Also, units

in which the rate constants are expressed differ from study to study. In some cases, the units do not take into consideration the reactant concentration (e.g.: l/g cat  $t$  and/or g/g cat  $t$ ), although a self-inhibiting effect of some reactants on their HDO is well documented. Most of the results on the HDO of the bio-oils are based on reactant disappearance rather than complete HDO. Thus, the stabilizing step is the primary objective, assuming that complete HDO will be achieved during the next step. The importance of catalyst structure on the relative HDO reactivities was recognized. Unless stated otherwise, the following general discus-

Table 18  
Summary of activation energies for bio-oil compounds

Reaction	Catalyst	Activation energy (kJ/mol)	Reference
GUA→Disappearance <sup>a</sup>	CoMo	58	[83]
GUA→Disappearance <sup>b</sup>	CoMo	111	[83]
GUA→Disappearance <sup>a</sup>	NiMo	71	[83]
GUA→Disappearance <sup>b</sup>	NiMo	112	[83]
GUA→CAT	CoMo	105	[81]
Catechol→Phenol	CoMo	122	[81]
4-MA→Methylethylbenzene	CoMo	50	[83]
4-MA→Methylethylbenzene	NiMo	73	[83]
DES→Disappearance	NiMo	104	[83]
DES→Disappearance	CoMo	108	[83]
ANI→Disappearance	CoMo	124	[102]

<sup>a</sup> Initial conversion.

<sup>b</sup> Middle conversion.

sion assumes HDO in the presence of sulphided conventional CoMo/Al<sub>2</sub>O<sub>3</sub> and/or NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts at temperatures, H<sub>2</sub> pressures and other conditions, which are typical of hydroprocessing operations. It is noted that the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst was found to be more acidic than the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst [107], i.e., the former has a higher cracking activity. Therefore, the type of catalyst used was always identified with the kinetic data in the preceding section.

Based on thermochemical considerations, the reactivity of the unsubstituted furanic rings will decrease in the following order: furan>BF>DBF. The experimental data obtained under similar conditions, which would confirm the same order, is lacking. Further, alkyl substitution of the furanic ring will change its reactivity. For example, in the case of furan, substitution in 2,5-positions will decrease the reactivity due to steric effects. However, experimental data showing the extent of the activity decrease is not available. Thus,

one may only speculate that 2,5-dialkyl furan will still be more reactive than the unsubstituted BF. Unsubstituted furan can be excluded from these considerations. Thus, it is unlikely that furan will be present in feeds to be hydroprocessed because of its high volatility (bp≈304 K). Uncertainties exist regarding the reactivity of BF, as indicated by the different values of the rate constants in Table 6. In this case, the different reactant concentrations used by different workers are the most probable contributor. Thus, Lee and Ollis [50] showed that, at 598 K, the rate constant decreased by half when the BF concentration increased from 0.15 to 0.25 mol/l. Yet, in the study of Edelman et al. [36], the reactant concentration was about 0.60 mol/l. In addition, the H<sub>2</sub>S concentration could approach 0.3 mol/l. Apparently, the sulphur concentration in feeds exceeding an optimal level is a cause of the inhibition of HDO sites by H<sub>2</sub>S [53].

In the study published by Böhringer and Schultz [106], the reactivity of unsubstituted BF and DBF was determined under the same conditions. They observed that the temperature at which 50% HDO was achieved was about 55 K higher for DBF than for BF. This was supported by the result published by Dolce et al. [108]. Girgis and Gates [60] showed that the ratio of the reactivity of DBT/DBF estimated from the overall conversion in a mixture with aromatics was about 12. However, when N-compounds and 5,6,7,8-tetrahydronaphthol were added, the ratio decreased to 3.6. In a neutral oil, this ratio was about 8 [97]. Using empirical rate constants for pure

Table 19  
Relative reactivities of O-compounds and/or groups [105]

	Temperature of iso-reactivity (K)	Activation energy (kJ/mol)
Ketone	476	12
Carboxylic	556	26
Methoxyphenol	574	27
4-Methylphenol	613	34
2-Ethylphenol	640	36
DBF	690	34

compounds obtained by Lee and Ollis [53], a DBT/BF value of 8.9 was obtained compared to about 3.0 for equimolar concentrations (0.15 mol/l) of the compounds. The value of 12 obtained for DBT/DBF by Girgis and Gates [60] confirms a lower reactivity of DBF compared to BF. However, the reactant concentrations and compositions of the mixtures were different. The DBT/BF and DBT/DBF ratio estimated from conversions observed by Rollman [61] for a mixture of compounds was 3.6 and 9.0, respectively, indicating a lower reactivity of DBF than BF. Thus, all evidence suggests that, over conventional hydroprocessing catalysts, the reactivity of the unsubstituted BF is greater than that of DBF when single compounds are considered.

For a novel catalyst, such as Mo<sub>2</sub>N, Abe and Bell [55] obtained a DBT/BF ratio of 0.9, in agreement with the results published by Ramanathan and Oyama [52]. However, the latter authors reported that, in the case of VN, the DBT/BF ratio was less than 0.1, indicating a superior HDO activity of the VN catalyst in comparison with the commercial NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. In the case of a V–Mo–O–N catalyst, the ratio of 0.8 was observed [109]. Therefore, the type and form of the catalyst has to be considered when comparing HDO reactivities of the O-compounds. It is obvious that a set of experiments still has to be designed and completed before the HDO reactivity of BF can be directly compared with that of DBF. The situation will become more complex when alkyl substituted BF and DBF will be compared. Nevertheless, the addition of an aromatic ring to a furanic ring will decrease the reactivity of the compound, suggesting that a true reactivity order will be similar to that established on the basis of thermochemical considerations. The ring substituted compounds of BF and DBF have not yet been studied. If the observation made by Gates and Topsøe [110] for sulphur analogs such as DBT applies also for DBF, the alkylation of the latter, particularly in 4- and 4,6-positions, would significantly diminish its HDO reactivity.

The database on the HDO reactivity of phenols is much more extensive than that on the furanic rings. The results in Table 10 [68] indicate the following order of reactivities of the methyl substituted phenols: *p*-methylphenol > *o*-methylphenol > 2,4-dimethylphenol > 2,6-dimethylphenol ~ 2,4,6-trimethylphenol. The pseudo-first-order rate constant for *p*-methylphenol

(Table 11), determined by Laurent and Delmon [71], is in the same range as that in Table 10. In another batch reactor study [65], a little difference between *m*- and *p*-methylphenol was observed, whereas *o*-methylphenol was the least reactive. However, the concentration of the reactants in hexadecane approached 60 mol%. Also, naphthalene was present and could interfere with the HDO. An important batch study on the HDO of phenols was conducted by Weigold [67] over a sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The results of this study (Table 20) are in qualitative agreement with other studies, although they were obtained during the HDO of pure phenols. Thus, in this case, a large self-inhibiting effect on HDO was present without any doubts. The usual order of reactivity, i.e., *m*-methylphenol > *p*-methylphenol > *o*-methylphenol, was established by Odebunmi and Ollis [62] in a continuous system. A low reactivity of the phenol compared to the substituted phenols is indicated by Weigold [67]. The results in Table 20 indicate a similar reactivity of the former as that of some *o*-substituted phenols, but much lower than that of *o*-cresol. Brendenberg et al. [86] observed that, at 598 K over an NiMo/Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>, the overall HDO of the phenol was about 17% compared to about 26% for the disappearance of *o*-cresol. However, in the latter case, phenol accounted for about 50% of the product. The results in Table 10 show that the pseudo-first-order rate constant for the HDO of the phenol is less than that of *o*-cresol. In the former case, the value was extrapolated from a low temperature region. It is noted that solid experimental data

Table 20  
Yield of aromatic hydrocarbons from phenols (sulphided CoMo/Al<sub>2</sub>O<sub>3</sub>, 573 K) [67]

Substrate	Product	Yield (wt.%)
Phenol	Benzene	8
<i>o</i> -Cresol	Toluene	19
<i>m</i> -Cresol	Toluene	48
<i>p</i> -Cresol	Toluene	23
3,4-Dimethylphenol	<i>o</i> -Xylene	45
3,5-Dimethylphenol	<i>m</i> -Xylene	31
2,3-Dimethylphenol	<i>o</i> -Xylene	13
2,4-Dimethylphenol	<i>m</i> -Xylene	7
2,5-Dimethylphenol	<i>p</i> -Xylene	10
2,3,5-Trimethylphenol	1,2,4-Trimethylbenzene	17
<i>o</i> -Ethylphenol	Ethylbenzene	<1

determining the reactivity of phenol relative to that of substituted phenols is still lacking. Based on this information, it is proposed that the reactivity of phenol is similar to that of *o*-substituted phenols. The adverse effect of *ortho*-substitution on the HDO rate is supported also by the results obtained by Gates et al. [7,20,21], shown in Table 12. This study is one of the few involving ring substituents other than methyl. Also, these authors showed that, in a weak acid fraction, 4-cyclohexylphenol was more reactive than both 1-naphthol and 5,6,7,8-tetrahydronaphthol, although the difference was small. An estimate of the rate constant for HDO of DBF in the neutral oil [98] gave a much lower value than that for naphthol. A similar estimate for BF is not available, raising some uncertainty in its reactivity relative to that of naphthol. However, a study of the HDO of BF in an equimolar mixture with DBT [53] showed that the HDS of the latter was two to three times faster than the HDO of BF. The relative HDS/HDO reactivity ratio of DBT and *m*-methylphenol, estimated under the same conditions, were also between 2 and 3 [63], indicating a similar overall HDO reactivity of BF and *m*-methylphenol in equimolar mixtures (0.15 mol/l) with DBT. In agreement with other observations, *o*-ethylphenol was less reactive than *m*-ethylphenol. Laurent and Delmon [71] showed that *o*-ethylphenol was much less reactive than *p*-methylphenol. As the results in Fig. 34 show, *o*-ethylphenol was more reactive than BF [51]. Apparently, this is the most convincing experimental evidence on the basis of which one may conclude that even the least reactive phenols, i.e., *o*-substituted phenols, are more reactive than unsubstituted BF when the overall HDO is considered.

A high HDO reactivity of ethers containing the C<sub>AL</sub>-O bond was indicated by Satterfield and Yang [51]. Kirby et al. [70] observed dinaphthylether to be more reactive than XA. However, in both cases, O-containing products were still present, particularly in the case of XA, i.e., 2-cyclohexylmethylphenol accounted for about half of the products. Nagai et al. [111] estimated the rate constants for the HDO of XA and the HDS of BT and DBT. The ratio of the rate constants, i.e., DBT/XA and BT/XA, is 0.64 and 0.90, respectively. However, the product distribution from the HDO of XA was not given. Thus, OH-containing intermediates, i.e., *o*-substituted phenol, may still have been present and as such govern the overall HDO.

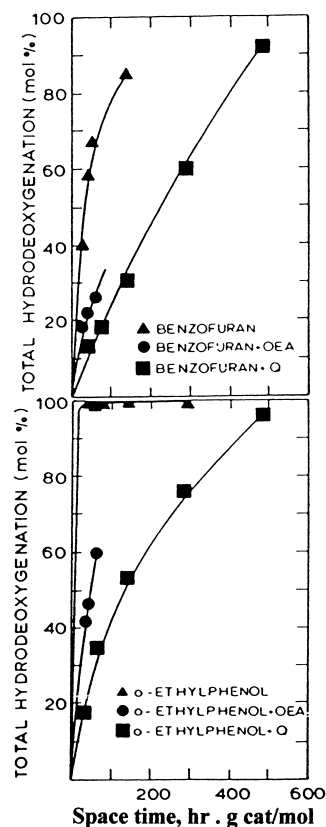


Fig. 34. Relative HDO reactivities for BF and *o*-ethylphenol alone and in the presence of quinoline (Q) and *o*-ethylaniiline (OEA) [51].

Petrocelli and Klein [81] observed similar rates for the overall HDO and conversion of *p*-substituted phenols to hydrocarbons as those for diphenylether to phenol and benzene. Therefore, with respect to the overall HDO, the diphenylether is considered to be less reactive than *p*-substituted phenols. Moreau et al. [112] compared the HDO of diphenylether with unsubstituted phenol, at 613 K and 7 MPa of H<sub>2</sub> over NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, and observed the latter to be about five times more reactive than diphenylether.

Based on the above discussion, the following tentative order of the HDO reactivity of O-containing groups can be established: alcohols > ketones > alkyl-ethers > carboxylic acids ≈ *m*- and *p*-phenols ≈ naphthol > phenol > diarylethers ≈ *o*-phenols ≈ alkylfurans > BFs > DBFs. There is little uncertainty in the order between alcohols up to carboxylic acids, even in the case of



complex mixtures. It is obvious that, in the same order, the amount of H<sub>2</sub> required to remove an O-containing group will be the largest for carboxylic acids, assuming its HYD to methyl group. This suggests that factors such as the catalyst activity, hydrogen availability, interaction with the catalyst surface etc. will be most important for carboxylic groups. In other words, the HDO reactivity of the carboxylic acids will be affected by the catalyst type and its deactivation to a greater extent than that of the more reactive groups. This is supported by the observation made by Laurent and Delmon [88] who reported that, under the same conditions, most of the DES was converted to O-compounds (monoester and acid), whereas most of the EDEC and DEC were converted to hydrocarbons, although the disappearance of the diester was much faster. Based on the observation made by Ledoux and Djellouli [107], the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst is more active for cracking than the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst, suggesting that the former will be more active for decarboxylation. However, the difference in activity may not be large enough to change the relative order of reactivities. There is some uncertainty in the above order about where to place arylothers because of their lesser sensitivity to the availability of H<sub>2</sub> for their overall HDO. Thus, at 673 K and 12.5 MPa of H<sub>2</sub>, phenols and carboxylic acids exhibited a similar reactivity [26]. Phenols are intermediates during the HDO of arylothers. It is believed that when H<sub>2</sub> availability becomes a factor, e.g., at a certain level of catalyst deactivation, the overall HDO of carboxylic acids may be slower than that of the phenols.

Studies on the HDO of bio-oils related compounds focussed mainly on the stabilization stage, i.e., only the disappearance of the reactant was followed. As the results in Table 21 show [86], phenols accounted for most of the disappeared GUA, in agreement with the results published by Laurent and Delmon [83]. Then, second stage treatment is required to complete the HDO. Little attention was paid to the HDO of the stabilized liquids. However, the established database on the HDO of phenols may be a basis for deducing information on the overall HDO reactivity of stabilized liquids, particularly if the phenols distribution in these liquids is known. Thus, while studying the HDO of a mixture of phenols, Li et al. [21] suggested that the overall HDO may be followed using one rate constant obtained as an average of the constants for

Table 21  
Product distribution (mol%) from reaction of GUA [86]

Temperature (K)	548	598
Conversion (%)		
Methylcyclohexane	<0.1	1.1
Cyclohexane	<0.1	0.3
Cyclohexene	<0.1	0.5
Benzene	<0.1	0.5
Toluene	<0.1	0.6
Phenol	30.9	53.5
Anisol	1.0	2.1
<i>o</i> -Cresol	3.2	9.4
<i>m</i> -Cresol	2.4	7.3
<i>p</i> -Cresol	0.8	1.6
Pyrocatechol	61.4	8.7

several phenols in the investigated mixture. Based on the kinetic analysis published by Laurent and Delmon [83,90], the following tentative order of the reactivity, defined as disappearance of the model compounds, can be established: 4MA≫DES≥GUA≫ANI. Based on the results in Table 14, the reactivity of GUA and DES is considered to be similar. The rate of disappearance of substituted GUAs (e.g., 4-methylGUA, euginol and vanillin) was compared by Petrocelli and Klein [81]. The differences in the pseudo-first-order rate constants for disappearance of these compounds indicate a similar reactivity for conversion to phenolic compounds and coke. The relative reactivity of the GUA and ANI is based on the results obtained by Hurf and Klein [102] rather than that of Bedenberg et al. [86], because in the latter case, a typical hydrocracking catalyst was used. In the case of the DES and 4MA, hydrocarbon products accounted for about 50 and almost 100%, respectively. The pseudo-first-order rate constants for the disappearance of EDEC and DEC at 553 K over an NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst were in the range of that for DES (Table 14), i.e.,  $9.1 \times 10^{-3}$  and  $4.6 \times 10^{-3}$  (min<sup>-1</sup> g cat), respectively. However, the yield of hydrocarbons was much greater than that for DES, indicating a larger overall HDO of EDEC and DEC than that of DES.

The available information on bio-oils related reactants allows some speculation on the overall HDO reactivities, i.e., assuming that the experiment would be performed in one stage to achieve a near complete HDO. In such a case, the overall HDO reactivities of EDEC and DEC are greater than that of DES because

of the greater conversion to hydrocarbons under the same conditions. The overall HDO reactivity of the GUA is lower than that of DES because, in the case of the former, phenols are the predominant primary products. In the former case, the HDO of hydroxyphenol and phenol will determine the overall HDO. Laurent et al. [82] showed that the conversion of the former to phenol is much faster than the conversion of phenol to hydrocarbons, suggesting that the latter reaction will determine the overall HDO, similar to the case of ANI [102]. Then, with respect to overall HDO, GUAs will be less reactive than *o*-phenols. A direct comparison of the HDO of furanic rings with GUAs would be required to determine the relative overall HDO reactivities. It is noted that this discussion is based on data obtained below 573 K. It is established that the HDO of phenols gains in importance with increasing temperature. This effect may change and/or diminish the relative HDO reactivities of the reactants. Other experimental parameters, e.g., contact time, H<sub>2</sub> availability etc., may be equally important.

### 7. Interaction of O-compounds with catalyst surface during HDO

The coordinatively unsaturated sites (CUS), or sulphur anion vacancies, which are located at the edges of MoS<sub>2</sub> slabs supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, are believed to be the sites for catalytic reactions during hydroprocessing. These sites can adsorb molecules with unpaired electrons such as NO, NH<sub>3</sub>, and pyridine, i.e., they have a Lewis acid character. The vacancies can consist of a significant fraction of the edge sulphur atoms. Double and even multiple vacancy centers can be present. The presence of Co and Ni does not affect the basic slab size of the MoS<sub>2</sub>. The Co or Ni does not appreciably increase the number of vacancies. However, the vacancies associated with Co or Ni are considerably more active than those associated with the MoS<sub>2</sub> alone. The vacancy concentration is thought to be a function of H<sub>2</sub> and H<sub>2</sub>S concentration. Then, the presence of H<sub>2</sub>O and O-containing compounds in the feed can change the catalyst structure, as well as the geometry of the vacancy if an insufficient amount of S-donating species is present in the feed. This was confirmed in the study on the deactivation of sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts during hydropro-

cessing of a coal-derived feed published by Yoshimura et al. [113]. However, an excess of sulphur may have an adverse effect on the overall HDO [53].

Interactions of the furanic rings with the catalyst surface are being frequently explained in relation to similar interactions of thiophenic rings. In fact, the generally accepted definition of the active site is based on evidence gathered during the HDS of the latter. Also, a mutual inhibition of HDS by O-compounds and that of HDO by S-compounds, observed by Odegunmi and Ollis [63], indicates a competitive adsorption at the same sites. In other words, the form and the geometry of the HDS sites and HDO sites are similar. This was also supported by the results of Yamamoto et al. [114], who observed that catalyst deactivation by coke had the same adverse effect on HDS and HDO. It is believed that, when a hydroaromatic hydrogen is involved, this similarity will remain unchanged during both HDS and HDO. Laurent and Delmon [71] speculated that the active site in C–O hydrogenolysis could be based on an ensemble of coordinatively unsaturated Mo atoms and the HYD sites on one triply unsaturated Mo atom. The H<sub>2</sub>S concentration influences the balance between these two types of sites. This speculation was in accordance with interpretations of the adsorption of dienes and thiophenic rings on MoS<sub>2</sub>, published by Kasztelan et al. [115] and Okamoto et al. [116], respectively. Girgis and Gates [60] discussed the interaction of DBF in relation to that of DBT. They proposed that, in the latter case, the interaction occurs through the bonding of C<sub>1</sub>–C<sub>2</sub> bond at an anion vacancy. This makes electron distribution around the sulphur more deficient. This promotes ring interaction with a surface sulphide anion. For furanic rings, similar electron distribution changes occur to a lesser extent because oxygen is much less polarizable than sulphur. This will weaken the adsorption of furanic rings on the catalyst surface. Thus, a higher H<sub>2</sub> pressure is required to achieve HDO conversion of DBF, similar to the HDS conversion of DBT.

In the case of BF, at least one adsorption mode may involve a bond via the C<sub>2</sub>–C<sub>3</sub> bond at the HYD site. This would yield 2,3-dihydroBF as an intermediate which will be subsequently converted to ethylphenol. Direct oxygen extrusion from BF (yielding styrene) may be favored by  $\sigma$ -bonded adsorption via an oxygen atom at the hydrogenolysis site. This is difficult to confirm experimentally because of the rapid removal

of the styrene product. Similarly, in the case of DBF, direct oxygen extrusion yielding non-hydrogenated products can arise from  $\sigma$ -bonded adsorption via an oxygen heteroatom. After the ring opening, the oxygen may still remain attached to the active site presumably as part of an OH group. Then, a non-hydrogenated product is released after OH elimination. The fully and/or partially hydrogenated products arise from  $\pi$ -bonded adsorption of the aromatic rings with the HYD sites. In this case, adsorption of the reactant has to compete with that of  $H_2$  at the same site. It is believed that such adsorption is more favorable for the formation of single-ring products during the HDO of DBF than that from  $\sigma$ -bonded adsorption.

The involvement of two distinct sites, i.e., one hydrogenolysis and the other HYD site, is being used to interpret the HDO of phenols. The former yields the parent aromatic as a primary product, whereas the HYD sites give cycloalkanes, presumably via an alcohol and/or ketone which cannot be detected because of rapid disappearance. These two routes arise from different reactant adsorption on the catalyst surface. While studying the HDO of phenols over sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts, Gevert et al. [68] proposed that the aromatic product can arise from  $\sigma$ -bonding adsorption through the oxygen atom, whereas the hydrogenated product arose from  $\pi$ -bonding adsorption through the benzene ring. The former is affected by 2,6-dialkyl substitution. Thus, Gevert et al. [100] showed that a triple anion vacancy site is required for a  $\sigma$ -bonding of 2,6-dimethylphenol, compared to a double vacancy site required for that of 3,5-dimethylphenol. In the case of  $\pi$ -bonding, the surface dimensions of both reactants were the same; therefore, steric effects cannot explain temperature effects on HYD ( $k_2$ ) shown in Fig. 30. Gevert et al. [100] suggested that differences in delocalized resonance effects arising from the position of methyl groups influenced the HYD route. The involvement of two distinct sites was supported by the strongly inhibiting effect of H<sub>2</sub>S on the path, giving aromatic products while hardly affecting the path yielding the hydrogenated product [68]. This observation is in agreement with the results published by Laurent and Delmon [71] for CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts. However, these authors observed that the inhibiting effect of H<sub>2</sub>S on the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst differed from that on CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The difference was attributed

to a greater proportion of hydrogenolysis sites on the latter compared to that on the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. Kallury et al. [92] attributed the difference between the reaction paths of *o*-dihydroxy benzene and that of *m*- and *p*-dihydroxybenzenes to different modes of adsorption on the catalyst surface. Thus, in the case of *o*-dihydroxybenzene, the O–O distance is similar as the Mo–Mo distance.

Interaction of bio-oil compounds with catalysts is less documented. In this regard, studies published by Delmon et al. [71,83,90,91,103] represent the most valuable source of information. They include 4MA, DES and GUA as well as H<sub>2</sub>O, which may be formed in large quantities. Special attention was paid to the effects of H<sub>2</sub>S and H<sub>2</sub>O on the catalyst activity as well [117].

In the case of 4MA, a small conversion to methylethyl benzene occurred even in the absence of catalysts [83]. The CoMo catalyst supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and/or carbon was much more active than unsupported CoMoS and that supported on SiO<sub>2</sub>. This is evidenced by the  $k_{4MA}$  in Table 15. The difference was attributed to a more efficient dispersion of MoS<sub>2</sub> on supports such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and carbon. This implies that the active sites for these reactions are situated on metal sulphides. This is supported by the absence of any poisoning effect of NH<sub>3</sub> on the HDO of 4MA. Apparently, the carbonyl group is adsorbed via its  $\pi$ -electrons. Two tentative routes were proposed. The first mode is based on the adsorption of the carbonyl carbon on a nucleophilic sulphur atom. The reaction then proceeds via addition of a proton to negative oxygen, and subsequently, the addition of a hydrogen atom to carbon. The second tentative mechanism proposed by Delmon et al. [90] involves reaction of the carbonyl group with an activated mobile hydridic species, so-called hydrogen spillover. The interaction of cyclohexanone with the surface of Ni<sub>3</sub>S<sub>2</sub> proposed by Olivas et al. [118] is shown in Fig. 35. They suggested that a similar interaction with SH groups attached to Mo may occur as well.

In the case of the DES, except for the potassium modified catalyst, all  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported catalysts had the highest decarboxylation and de-esterification activities, whereas SiO<sub>2</sub> supported catalysts had a negligible decarboxylation activity but relatively important de-esterification activity. Carbon-supported catalyst had a moderate decarboxylation activity and

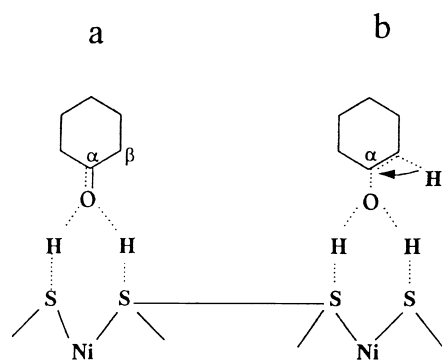


Fig. 35. Adsorption mode of phenol at  $\text{Ni}_3\text{S}_2$  [118].

a low de-esterification activity. Thus, the most active catalysts were those with the highest surface acidity, suggesting its role during decarboxylation reactions. It was proposed that decarboxylation may involve an addition of a proton to one of the oxygens of the carboxylic group, followed by elimination of the latter. The  $\gamma\text{-Al}_2\text{O}_3$  alone had no activity for decarboxylation and HYD, but exhibited some activity for de-esterification. Apparently,  $\gamma\text{-Al}_2\text{O}_3$  is able to add OH groups to electrophilic carbons [119]. The unsupported CoMoS had no activity for decarboxylation. Based on these facts, Delmon et al. [91] concluded that active sites for decarboxylation could correspond to metal sulphides bound to  $\gamma\text{-Al}_2\text{O}_3$ , presumably Brønsted acid sites. This is supported by a strong inhibition of decarboxylation reactions by  $\text{NH}_3$  [90] and potassium (Table 14). The decarboxylation was poisoned by  $\text{NH}_3$  to a greater extent than HYD, suggesting a difference in the acidity of the sites involved. The  $\text{H}_2\text{S}$  had a beneficial effect on decarboxylation and HYD, especially for the  $\text{NiMo}/\text{Al}_2\text{O}_3$  catalyst. It is suggested that  $\text{H}_2\text{S}$  facilitated SH groups which are considered to be a source of protons [120]. This could be more evidence for proton participation during DES reactions.

Comparison of the results in Tables 15 and 16, particularly a low coke formation on unsupported as well as on carbon- and  $\text{SiO}_2$ -supported catalysts compared with the  $\gamma\text{-Al}_2\text{O}_3$  supported catalysts, shows that the acidity was involved both in the conversion of GUA to CAT and phenol, as well as to coke. The first step in the reaction of GUA involving demethylation was not inhibited by  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ , but strongly inhibited by  $\text{NH}_3$ . At 573 K,  $\gamma\text{-Al}_2\text{O}_3$  alone had about half ac-

tivity for demethylation as that of the catalyst. The strong poisoning by  $\text{NH}_3$  suggests that Lewis acids on  $\gamma\text{-Al}_2\text{O}_3$  may be catalytic sites for demethylation. The subsequent reaction sequence involving the conversion of CAT to phenol and finally to benzene required the presence of a catalyst. This sequence was inhibited by  $\text{H}_2\text{S}$ , in a manner similar to the inhibition of the HDO route of phenols leading to alkylbenzenes. Then, catalytic sites for the demethylation may be associated with the support, whereas those for dehydroxylation are associated with the metal sulphides in a similar manner as discussed in the case of phenols. Bredenberg et al. [86] proposed that demethylation can occur on both support and metal sulphides involving different mechanisms, i.e., homolytic splitting on metal sulphides and a heterolytic scission on the support. Also, these authors proposed the formation of a strong bond between the phenolic hydroxy groups and basic OH groups on the support as the reason for the lower reactivity of GUA compared to ANI.

## 8. HDO of real feeds

Extensive information on the hydroprocessing of real feeds can be found in the literature. However, because most of the attention has been paid to HDS, HDN, HDM, HYD and hydrocracking, the content of oxygen and the type of O-containing compounds in the feeds and products are not even reported. In a few studies, the O content is reported but it was determined by the difference rather than direct analysis. Also, it is not clear whether all precautions were taken to avoid contact of the feeds and products with air. Then, the autoxidation of hydrocarbons could affect the determination of the overall HDO. Moreover, part of the  $\text{H}_2\text{O}$  formed on HDO may remain dissolved in the products, and as such affect the overall HDO determination, indicating a need for drying the products prior to the analysis. It is not always clear from the published studies that these and other relevant issues were addressed. This suggests that studies in which the content of O-containing compounds and/or groups in the feeds and products were determined provide a reliable source of information on the extent of HDO. Studies on single model compounds and mixtures of model compounds indicated the presence of self-inhibition, inhibition and poisoning effects. It was shown earlier

that an accurate account of these effects can only be obtained for single reactants and simple mixtures. In the case of real feeds, these effects are rather complex and only some general trends may be established from the relative removal of heteroatoms. All available information shows that HDS is much greater than HDN and HDO. However, the relative rates of HDN and HDO are not clearly established.

On account of a low O content, little information is available on the HDO of fractions derived from conventional crudes. One of the first studies on the HDO

of real feeds involved a gas oil derived from heavy oil by thermal hydrocracking. The content of S, N and O in the feed was 3.69, 0.39 and 0.44 wt.%, respectively. The work was performed at 673 K over a sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst and H<sub>2</sub> pressure of 13.7 MPa [121]. In this case, the O content was determined by neutron activation analysis and acid numbers by KOH titration. The increase in the acid number with increasing Mo content of the catalyst, in Fig. 36, was attributed to the conversion of neutral BFs to acidic phenols. This study was expanded to include simul-

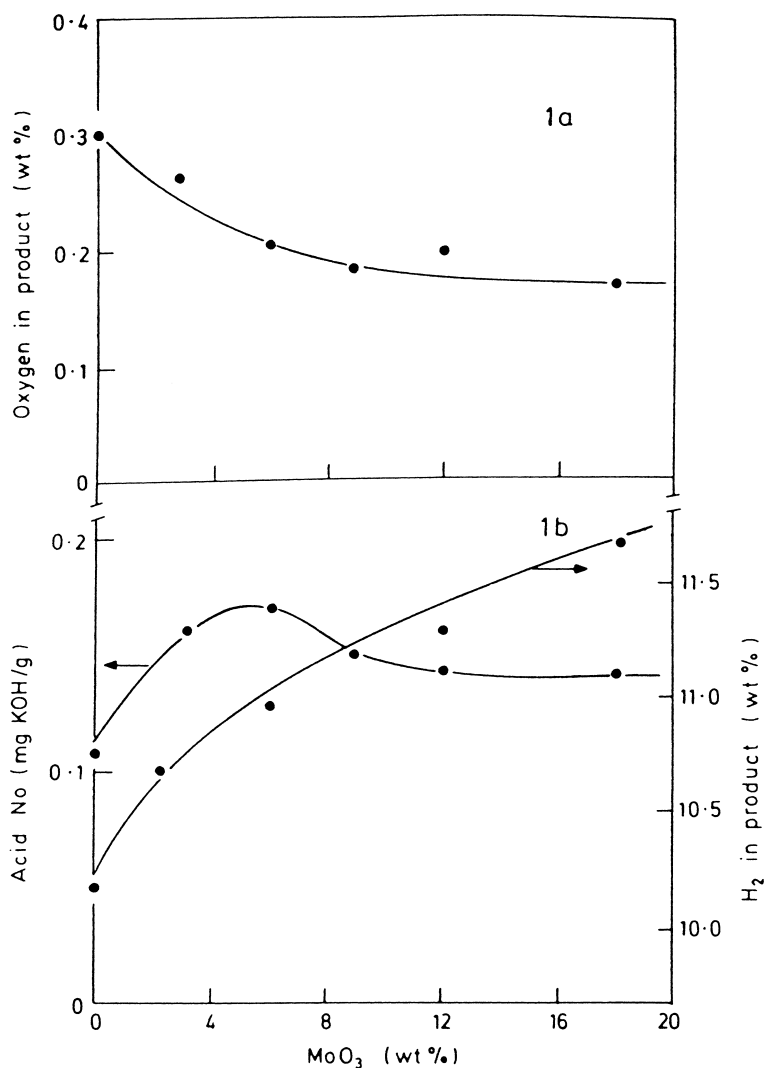


Fig. 36. Effect of MoO<sub>3</sub> content on O removal (1a) and acid No. (1b) during HDO of gas oil [121].

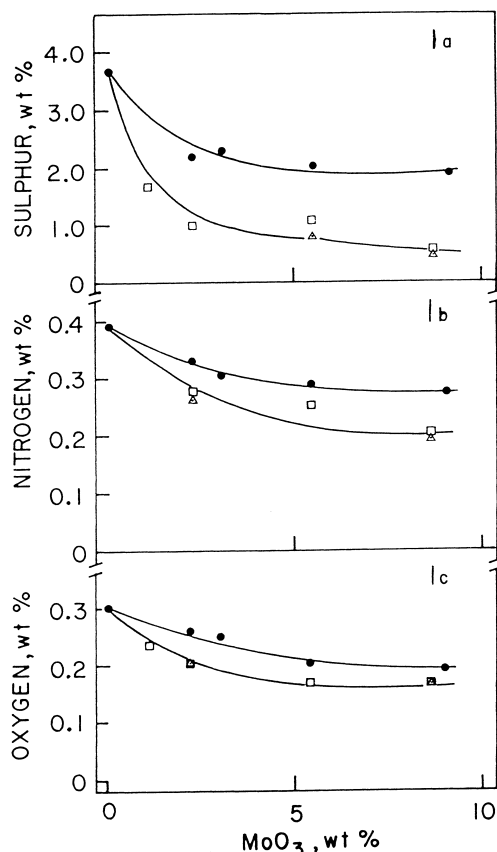


Fig. 37. Effect of  $\text{MoO}_3$  content on removal of S (1a), N (1b) and O (1c) during HDO of gas oil [122].

taneous removal of S, N and O [122]. A summary of these results is given in Fig. 37. Based on these results, the following order of the relative removal of heteroatoms was established:  $\text{HDS} > \text{HDN} > \text{HDO}$ . It was proposed that the greater strength of the  $\text{C}_{\text{AR}}\text{-OH}$  bond, compared to that of the  $\text{C}_{\text{AR}}\text{-NH}_2$  bond, may be responsible for the lower HDO than HDN. Thus, the high temperature and the high  $\text{H}_2$  pressure used would favor a rapid heteroring opening, suggesting that aromatic amines and phenols may have governed the overall HDN and HDO, respectively.

HDO is among the key reactions occurring during the upgrading of CDLs. In this regard, an extensive evaluation was undertaken by Gates et al. [16–20]. It is noted that, in these studies, the feeds were diluted in a solvent. The effect of temperature on upgrading a SRC distillate (bp 503–728 K) was investigated

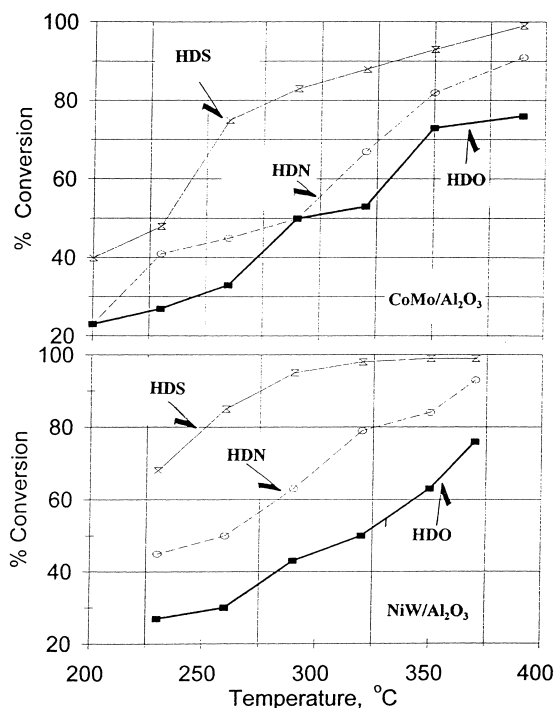


Fig. 38. Effect of temperature on HDS, HDN and HDO of SCR liquid [123].

by Dalling et al. [123] over sulphided  $\text{CoMo}/\text{Al}_2\text{O}_3$  and  $\text{NiW}/\text{Al}_2\text{O}_3$  catalysts in a semibatch reactor at 12 MPa  $\text{H}_2$  pressure. The content of S, N and O in the feed was 0.4, 2.2 and 3.0 wt.%, respectively. The results from this study are shown in Fig. 38. The order of heteroatom removal agrees with that for gas oil [122], i.e.,  $\text{HDS} > \text{HDN} > \text{HDO}$ . However, with respect to the absolute amount of the heteroatom removed, HDN and HDO were similar. Yoshimura et al. [124] used a sulphided  $\text{NiMo}/\text{Al}_2\text{O}_3$  catalyst for upgrading a hexane-soluble oil obtained from a CDL in a batch reactor at 673 K. The content of S, N and O was 0.27, 0.61 and 2.8 wt.%, respectively. In this case, the overall HDO conversion was slightly greater than the HDN conversion, although the absolute amount of O removed was significantly greater than that of N. However, HDN was affected by catalyst deactivation to a much greater extent than HDO. In qualitative terms, these results agree with those published by Sato [125], who observed that DBFs accounted for most of the O-containing compounds in the products, confirming

Table 22  
Activation energies (kJ/mol) for HDN, HDS and HDO of coal-derived feed [126]

Feed	Catalyst	$E_{\text{HDN}}$	$E_{\text{HDS}}$	$E_{\text{HDO}}$
Illinois 6	Co–Mo	49	31	48
Illinois 6	Ni–W	50	36	35
Illinois 6	Ni–Mo	48	42	38
Black Thunder	Co–Mo	33	45	19
Black Thunder	Ni–W	40	41	20

their low reactivity. Perhaps, the most detailed study on the relative removal of heteroatoms from CDLs was published by Davis et al. [126], who used two naphtha samples derived from Illinois 6 and Black Thunder coals. The activation energies obtained between 493 and 673 K are shown in Table 22. In every case, HDS was greater than HDN and HDO. However, among five cases involving different combinations of catalyst and naphtha, in one case HDN>HDO, two cases HDN≈HDO and for two cases HDO>HDN. These results [126] can be used to illustrate the effects of catalyst type and feed origin on the relative removal of heteroatoms. In the subsequent study, Davis et al. [127] used the second row transition metal sulphides

for hydroprocessing a CDL containing 820 ppm, 1420 ppm and 1.24 wt.% of S, N and O, respectively, between 548 and 673 K and 4.7 MPa of H<sub>2</sub>. Relative activities of these sulphides for HDS, HDN and HDO are shown in Fig. 39. It is evident that RuS<sub>2</sub> exhibited the highest activity for HDN followed by HDS and HDO, whereas for the other sulphides, the following order was established; HDS>HDO>HDN. Song et al. [128] used several NiMo catalysts of similar chemical composition but different mean pore diameter and identified pore size ranges which are optimal for HDO of heavy feed derived from coal.

Hydroprocessing of the feeds derived from various oil shales was reviewed in detail by Landau [104], who established the following order for overall heteroatom removal: HDS>HDO>HDN. This is supported by the results published by Holmes and Thomas [129]. These authors hydroprocessed the crude obtained from Paraho oil shale over a sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst at about 673 K. The feed contained 0.7, 2.0 and 2.2 wt.% of S, O and N, respectively. In this case, almost complete removal of S was achieved, whereas that of O and N was 95 and 80%, respectively. Under similar conditions, Afonso et al. [26] obtained about

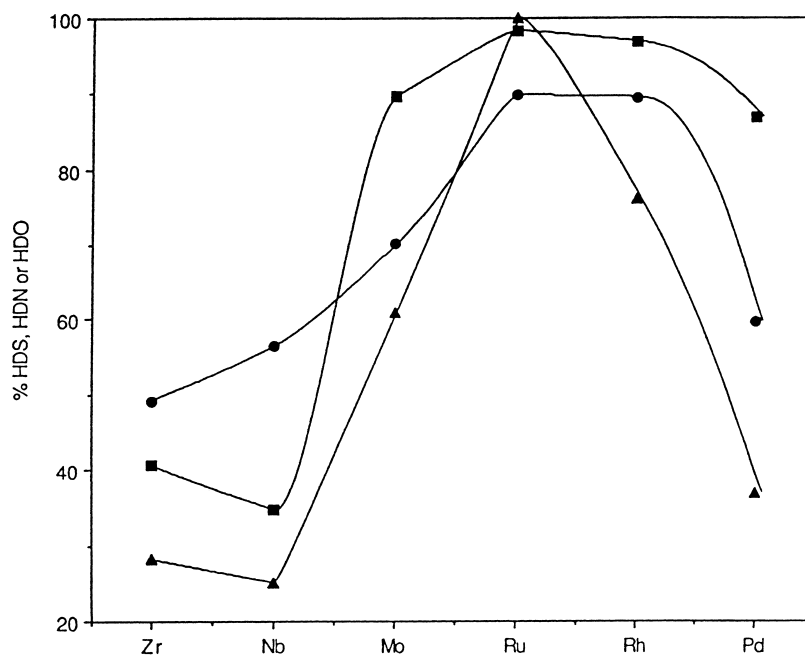


Fig. 39. Simultaneous HDS (■), HDN (▲) and HDO (●) of coal-derived naphtha over metal sulfides [127].

87 wt.% removal of O, whereas S and N were not analyzed. Although the information is limited, it is evident that the relative rates of heteroatom removal from oil shale-derived feeds differ from those established above. This is not surprising when the type and amount of O- and N-containing compounds in the feeds are taken into consideration. Thus, it was reported that the least reactive O-compounds in Rundle oil shale were phenolics (not heterocyclics), whereas the least reactive N-compounds were heterocyclics [25,130]. In such a case, the removal of O will be easier than that of N because phenols are much more reactive than furans.

The conditions employed during the upgrading of bio-oils depend on their origin. Thus, a review of the processes [29] indicates a wide range of liquid product compositions, although the processes can be divided into two general groups, i.e., high pressure liquefaction and pyrolysis. In the latter case, the liquids have a higher O content and are less stable than those derived by high pressure liquefaction. Primary products from liquefaction may require pretreatment, such as extraction and/or desalting prior to their upgrading step. However, as indicated by Goudriaan and Peferoen [131], substantial HDO conversion of such liquids can be achieved in one stage. In most cases, HDS and HDN play a minor role during the upgrading because of a very low content of S and N (usually less than 0.1 wt.%) in the bio-oils. More than 95% O removal from a high pressure wood liquefaction product, containing about 15 wt.% O, was achieved over a sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst at 573 K [132]. Using the same bio-oil, Gevert et al. [133] studied the effect of pore diameter of a sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst on the overall HDO. Continuous catalyst deactivation was observed during hydroprocessing of bio-oil from liquefaction [134]. However, as is shown in Fig. 40 [135], after the same feed was desalted, the deactivation was only observed during the initial stages, followed by steady-state HDO. The best performance was achieved at 623 K for the catalyst with narrow pores. Conditions, which are typical of cracking, i.e., near atmospheric pressure and zeolite type catalysts, were also used for the upgrading of the bio-oils from liquefaction [136–138]. A detailed account of the upgrading of bio-oils from pyrolysis and liquefaction was given by Elliott and Baker [139,140]. A substantial upgrading of a liquefaction bio-oil over a sulphided

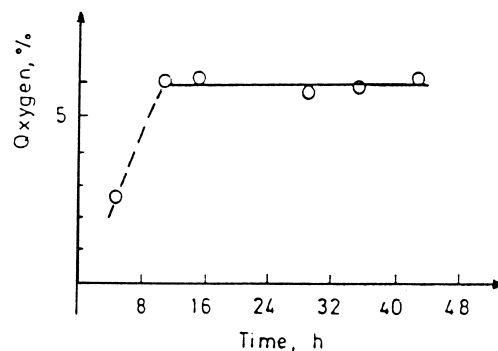


Fig. 40. Oxygen content as function of time [135].

CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst at about 673 K was achieved. In this case, the O was almost completely removed from the feed. However, two upgrading stages were required for the pyrolysis oil. The first stage could be performed below 573 K because of rapid catalyst deactivation at higher temperatures. The second stage was conducted at 626 K. The O content was decreased from 52.6 wt.% to 32.7 and 2.3 wt.% in the first and second stages, respectively. Churin et al. [141] studied upgrading of the bio-oil produced by pyrolysis of wastes from the olive oil industry. The feed contained 15.3 and 3.3 wt.% of O and N, respectively. In spite of relatively low O content, two stages were required for upgrading. In the first stage, which was performed at 573 K and 12 MPa of H<sub>2</sub>, about 64 and 24% of O and N, respectively, was removed over a CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst, whereas about 69 and 58% of O and N, respectively, was removed over an NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The upgrading was completed at 673 K. Rocha et al. [142] evaluated a two-stage process involving hydroprocessing of cellulose in the first stage, followed by hydroprocessing of the primary products still in a vapor phase, in the second stage. The H<sub>2</sub> pressure varied between between 0.5 and 10 MPa. In this case, the fixed bed of a presulphided NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst was above the pyrolysis zone. The O content of the liquids after one- and two-stage processing was 19 and 9 wt.%, respectively. Polymerization occurring during the upgrading of bio-oil from vacuum pyrolysis was reported by Gagnon and Kaliaguine [143]. Thus, a molecular weight increase of the product was observed already during pretreatment over an Ru/Al<sub>2</sub>O<sub>3</sub> catalyst at 353 K and 4.2 MPa of H<sub>2</sub>. Polymerization



was more evident during the subsequent upgrading in the presence of an NiWO/Al<sub>2</sub>O<sub>3</sub> catalyst at 598 K and about 18 MPa of H<sub>2</sub>, although significant O removal was achieved.

Apparently, the chemical composition of the feed is one of the factors determining the relative removal of S, N and O during hydroprocessing. In fact, it may change the generally accepted order, i.e., HDS>HDO>HDN. For example, if in a feed, the least reactive O-compounds (DBFs) are predominant, together with more reactive N-compounds (quinolines), the overall HDN may be greater than the overall HDO [106,144]. Carbazoles appear to be the least reactive N-compounds [106]. However, their boiling point is significantly greater than that of DBFs, suggesting that the occurrence of the latter together with more volatile quinolines in the same feed is possible. Catalysts can have a significant effect on the relative heteroatom removal. The study conducted in the presence of an in-situ produced MoS<sub>2</sub>, published by Ting et al. [145], represents one extreme. In this case, the following order was established: HDS≈HDN≫HDO. Another extreme is the study in which HDO was about 10 times greater than HDS in the presence of a VN catalyst [52].

## 9. Conclusions

A wealth of information on the origin of O-compounds in various feeds has been established. The HDO of a wide range of feeds consisting of the single model O-compounds, their mixtures with S- and N-compounds as well as real feeds have been studied under different experimental conditions. The mechanism of the single O-compounds can now be described accurately including their self-inhibiting effects, as well as the inhibiting and poisoning effects of S- and N-compounds, respectively. The effect of the O-compounds on HDS and HDN has been studied as well. Information is available on the effect of the main HDO product, such as H<sub>2</sub>O on the catalyst surface, including its effect on the overall HDO, HDS and HDN.

The complexity of HDO depends on the feed origin. HDO plays a minor role during the hydroprocessing of conventional crudes, whereas its role during that of the CDLs is rather major. Hydroprocessing

of the latter is now understood to the point that the production of commercial fuels can be undertaken, providing that the economics are favorable. Much less information is available on the HDO of the oil shale-derived feeds, particularly, the presence of the carboxylic groups-containing compounds, which are resistant to HDO, requires additional attention. With respect to HDO, the most complex feeds are those derived from biomass. In this regard, in recent years, the hydroprocessing of bio-oils has been receiving most of the attention.

Some uncertainties in establishing the order of the relative HDO reactivities of the O-compounds and/or groups of the compounds still exist. In most cases, the results published by different authors were obtained under the different experimental conditions. This prevents direct comparison of the results. Even for a single O-compound, reactivity is influenced by the type of solvent used and the reactant concentration because of the self-inhibiting effects. Complications arise when the results obtained for single-model compounds are compared with those obtained for the same compounds in the various mixtures because of the mutual inhibiting and poisoning effects. The activation energies for some model compounds indicate that their relative reactivities may change with temperature. The type of catalyst is another factor influencing the relative HDO reactivities. It appears that differences in the relative HDO reactivities reported by different authors can be rationalized by thoroughly evaluating the experimental parameters used. Significant efforts would be required to obtain additional database for establishing a more accurate order of the relative HDO reactivities. In view of others priorities in the catalysis research, it is not certain whether it would be worthwhile to undertake such a task.

It is generally accepted that the relative removal of heteroatoms during hydroprocessing occurs in the following order: HDS>HDO>HDN. This is true for the feeds in which analogous S-, O- and N-containing compounds predominate. However, a different order, e.g., HDS>HDN>HDO, was also observed and can be explained by the presence of the least reactive O-compounds (furanic rings) together with more reactive N-compounds (quinolines) in the feed. Such a situation is not unusual when boiling points of the single O- and N-compounds are taken into consideration. Thus, based on the boiling points, a naphtha and/or

light gas oil could have a high content of DBFs and quinolines and a low content of the carbazoles which are the least reactive N-compounds. The type of catalyst used can influence the relative heteroatom removal as well. For example, novel catalysts, possessing about 10 times higher activity for C–O bond (in BF) hydrogenolysis than that for the C–S bond (BT) hydrogenolysis have been tested.

The upgrading of bio-oils remains the primary area of the current interests in HDO. It is believed that breakthroughs in the catalyst development may be required to make this source of fuels more attractive. Other than Mo, W based catalysts may be more suitable as it is already indicated by some preliminary information. For bio-oils from pyrolysis, an additional (HYD) stage may be needed because of a high aromatics content of products after a two-stage upgrading. It is evident that a complete HDO is the main objective of the second upgrading stage conducted under typical hydroprocessing conditions. It is believed that the feed pretreatment (e.g., dewatering, desalting etc.) prior to upgrading is not receiving adequate attention, although it may slow down catalyst deactivation. The production of fuels from bio-oils may be looked at from another point of view. Thus, it may be at least a partial answer to the environmental problems associated with the storage and disposal of biomass.

## 10. List of symbols

ANI	Anisol
BF	Benzofuran
BT	Benzothiophene
CAT	Catechol
CDL	Coal-derived liquid
CUS	Coordinatively unsaturated sites
DBF	Dibenzofuran
DBT	Dibenzothiophene
DEC	Decanoic acid
DES	Diethylsebacate
EDEC	Ethyldecanoate
EDS	Exxon donor solvent
GUA	Guaiacol
HDM	Hydrodemetallization
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HYD	Hydrogenation

4MA	4-Methylacetophenone
SRC	Solvent refined coal
XA	Xanthene
THF	Tetrahydrofuran

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