f_M	major frequency	U	superficial gas velocity (m/s)
g	acceleration	U_{mf}	minimum superficial fluidization gas velocity (m/s)
H	vertical distance above gas distributor (mm)	U/U_{mf}	fluidization number
L	height of a bed section (m)	Z	excess air values
T_B	bed temperature		
T_1	bed temperature at a given distance above the distributor plate (K)		

Reactions of Model Compounds in the Presence of Pyrene and MoS_2 To Simulate Coprocessing

Ping-Shun Ting,[†] Christine W. Curtis,[*,†] and Donald C. Cronauer[‡]

*Chemical Engineering Department, Auburn University, Auburn University,
Alabama 36849-5127, and Amoco Oil Company, Naperville, Illinois 60566*

Catalytic reactions of pyrene using in situ generated MoS_2 from molybdenum naphthenate and excess sulfur were evaluated in the presence of added model species, both hydrocarbons and heteroatomic species. The added hydrocarbons and heteroatomic compounds containing oxygen and sulfur had little effect on the hydrogenation of pyrene at either 400 or 425 °C, but quinoline at 400 °C reduced the hydrogenation of pyrene by half. Reactions at 425 °C also reduced the hydrogenation of pyrene by half regardless of the added model species. The added model species underwent different degrees of reaction: the hydrocarbons underwent little or no reaction, dibenzofuran showed little hydrodeoxygenation, dibenzothiophene yielded substantial hydrodesulfurization, and quinoline was almost totally hydrodenitrogenated. The addition of quinoline at increasing concentration resulted in substantial lowering of pyrene hydrogenation and quinoline hydrodenitrogenation. Introduction of quinoline at a low concentration of 0.4 wt % gave a pyrene hydrogenation rate constant of 0.073 min^{-1} at 400 °C while an increase in quinoline to 10.0 wt % yielded a rate constant of 0.020 min^{-1}.

Introduction

Coprocessing is the simultaneous processing of coal and petroleum residuum with the objective of liquefying coal and hydrogenating and removing heteroatoms from the coal-derived liquids and the resid.[1-5] The primary advantage of coprocessing technology is that the process offers a bridge from the present petroleum-based technology to a synthetic fuel coal-based technology. For coprocessing to be an efficient process, the reactions between the coal and resid must be known and the influence of the catalyst on these systems determined. Therefore, the mechanisms and reactions of coprocessing must be understood on a fundamental basis for the process to be performed most effectively.

The objectives of this research are to understand fundamentally and mechanistically specific reactions that occur during coprocessing using a finely divided catalyst. Although the reactions involved in coprocessing are very complex, the primary reactions involve the hydrogenation of multiring aromatics and the removal of the heteroatoms from both coal and resid. The heteroatomic species from the resid and coal contain oxygen, nitrogen, and sulfur which are removed as H_2O, NH_3, and H_2S, respectively. Model compounds were selected to represent the types of species present in the coal–resid coprocessing system and to evaluate the reactions that occur in the presence of an

in situ sulfided molybdenum naphthenate catalyst precursor which forms MoS_2 under the reaction conditions utilized.[6] Models were chosen to elucidate the reaction mechanisms since the effect of catalysts could be readily evaluated. This simplification of the coprocessing system is helpful because the complexity of the interactions between coal and resid frequently tends to make discerning the underlying mechanisms difficult.

The models selected for this study were pyrene, representing polynuclear aromatic compounds; perhydropyrene, multiring naphthenes; tetralin, hydroaromatic compounds; dibenzothiophene, sulfur-containing species; dibenzofuran, etheric oxygen-containing species; quinoline, nitrogen-containing species; amylcyclohexane and 1-phenyl-undecane, cyclohexyl and phenyl species with long aliphatic side chains in petroleum residuum. These species were chosen because of their prevalence as compound types in either coal liquids or resids. Pyrene was selected as the probe species to evaluate the effect of the other components on its hydrogenation in the presence of in situ generated MoS_2. Pyrene has previously been studied thermodynamically and kinetically as well as evaluated as a

---

*Author to whom correspondence should be addressed.
†Auburn University.
‡Amoco Oil Co.

(1) Monnier, J. *CANMET Rep.* March 1983, No. 84-5E.
(2) Gleim, W. K. T., U.S. Patent 4,306,960 (1980).
(3) Rosenthal, J. W.; Dahlberg, A. J. U.S. Patent 4,330,390 (1982).
(4) Audeh, C. A. U.S. Patent 4,379,045 (1983).
(5) Yan, T. Y.; Espenscheid, W. F. *Fuel Process. Technol.* 1983, 7, 121–133.
(6) Kim, H.; Curtis, C. W.; Cronauer, D. C.; Sajkowski, D. J. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* 1989, 34(4), 1431.

Table I. Catalytic Hydrogenation of Pyrene in the Presence of Other Species with in Situ Generated MoS₂

| | | | | product distribution of pyrene, mol % | | unknown | | | |
	PY[a]	DHP	THP	HHP	HHP*	1	2	DCHP	% HYD[b,c]
					400 °C				
PY/none	8.1 ± 0.1	12.9 ± 0.2	5.2 ± 0.1	24.6 ± 0.2	16.2 ± 0.1	14.3 ± 0.2	7.8 ± 0.1	10.9 ± 0.1	38.9 ± 0.1
PY/QUI	28.1 ± 1.2	34.0 ± 2.0	10.3 ± 0.8	16.0 ± 0.5	9.0 ± 0.9	1.0 ± 1.0	1.6 ± 1.0	trace	17.9 ± 1.7
PY/TET	9.1	14.6	4.1	23.9	16.0	12.2	8.3	11.8	38.0
PY/DBT	9.7 ± 0.4	14.1 ± 0.5	4.3 ± 0.1	24.8 ± 0.2	16.6 ± 0.1	11.6 ± 0.1	8.0 ± 0.2	10.9 ± 0.2	37.5 ± 0.4
PY/DBF	8.9 ± 0.3	14.6 ± 0.1	4.6 ± 0.1	24.2 ± 0.2	15.5 ± 0.3	12.2 ± 0.4	8.4 ± 0.2	11.6 ± 0.2	38.0 ± 0.3
					425 °C				
PY/none	31.4 ± 1.4	20.8 ± 0.1	4.8 ± 0.1	17.4 ± 0.4	11.0 ± 0.3	5.4 ± 0.1	4.3 ± 0.1	4.9 ± 0.2	23.6 ± 0.5
PY/QUI	32.0 ± 1.4	25.0 ± 0.6	4.8 ± 0.1	16.8 ± 0.1	11.4 ± 0.5	4.0 ± 0.5	2.4 ± 0.3	3.6 ± 0.6	21.1 ± 1.0
PY/TET	30.1 ± 2.2	24.2 ± 0.5	4.8 ± 0.0	17.0 ± 0.7	12.2 ± 0.6	4.7 ± 0.6	3.0 ± 0.3	4.0 ± 0.5	22.5 ± 1.3
PY/DBT	29.2 ± 3.3	24.8 ± 1.4	5.2 ± 0.0	16.4 ± 1.6	11.5 ± 1.3	5.1 ± 0.7	3.3 ± 0.5	4.5 ± 0.5	22.9 ± 2.0
PY/DBF	30.8 ± 0.1	24.3 ± 0.1	5.0 ± 0.1	16.9 ± 0.6	12.4 ± 0.2	4.2 ± 0.3	2.8 ± 0.1	3.6 ± 0.3	21.8 ± 0.2

[a] PY (pyrene), DHP (dihydropyrene), THP (tetrahydropyrene), HHP (hexahydropyrene), HHP* (another isomer of HHP), DCHP (decahydropyrene), unknowns 1 and 2 (most probably isomers of DCHP), TET (tetralin), QUI (quinoline), DBF (dibenzofuran), DBT (dibenzothiophene). [b] HYD = hydrogenation. [c] For the calculation of percent hydrogenation, perhydropyrene was used as the most hydrogenated liquid product.

species for hydrogen shuttling in coal liquefaction.[7-9,12,14] This current investigation took these studies one step further and reacted pyrene thermally and catalytically in the presence of naphthenes and heteroatomic compounds. A kinetic study was also undertaken that measured the effect of a nitrogen-containing compound on the activity of the finely divided MoS₂ catalyst.

Experimental Section

Chemicals and Catalyst. Pyrene, perhydropyrene, amylcyclohexane, 1-phenylundecane, dibenzofuran, dibenzothiophene, tetralin, and quinoline were purchased from Aldrich Chemical. They had purities greater than 98% and were used as received. Molybdenum naphthenate, an oil-soluble catalyst with a Mo content of 6 wt %, was obtained from Shepherd Chemical Co. and was used as received. A table of nomenclature is included to present the symbols used to designate reaction products and intermediates.

Reactions and Analyses. Batch hydrogenation reactions were performed in stainless steel tubular microreactors that had a volume of approximately 21 mL, were oriented horizontally, and were agitated at 550 cpm. The reaction conditions were temperatures of 400 or 425 °C, hydrogen pressure of 1250 psig at ambient temperature and reaction time of 30 min. The reactants were typically introduced at 1 wt % each, in a total charge of 4 g of solution. The solvent was *n*-hexadecane that hydrocracked 1-2% at the conditions of this study. The catalyst was an oil-soluble molybdenum naphthenate that was sulfided in situ by elemental sulfur present in a 3:1 S to Mo ratio by weight. MoS₂ of small particle size and relatively high surface area[6] was formed. Most catalytic reactions were at least duplicated.

Liquid products from the reactor were washed with tetrahydrofuran and analyzed by gas chromatography using a Varian 3400 gas chromatograph with a SGE HT-5 Al-clad column and FID detection. The column was maintained at 60 °C for 2 min after injecting the sample and then temperature-programmed from 60 to 240 °C at a rate of 3 °C/min. The samples were quantified by using the internal standard method with *p*-xylene as an internal standard. Reaction products were identified by comparing retention times with authentic compounds and by gas chromatography/mass spectrometry using a VG 70 EHF.

(7) Stephens, H. P.; Kottenstette, R. J. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* 1985, 30(2), 345–353.
(8) Johnston, K. P. *Fuel* 1984, 63, 463–468.
(9) Shaw, R.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* 1977, 81, 1716–1729.
(10) Kim, H.; Curtis, C. W. *Energy Fuels* 1990, 4, 206–214.
(11) Kim, H.; Curtis, C. W. *Energy Fuels* 1990, 4, 214–219.
(12) Shabtai, J.; Veluswamy, L.; Oblad, A. G. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* 1978, 23(1), 107–113.
(13) Frye, C. E. *J. Chem. Eng. Data* 1962, 7, 592–595.
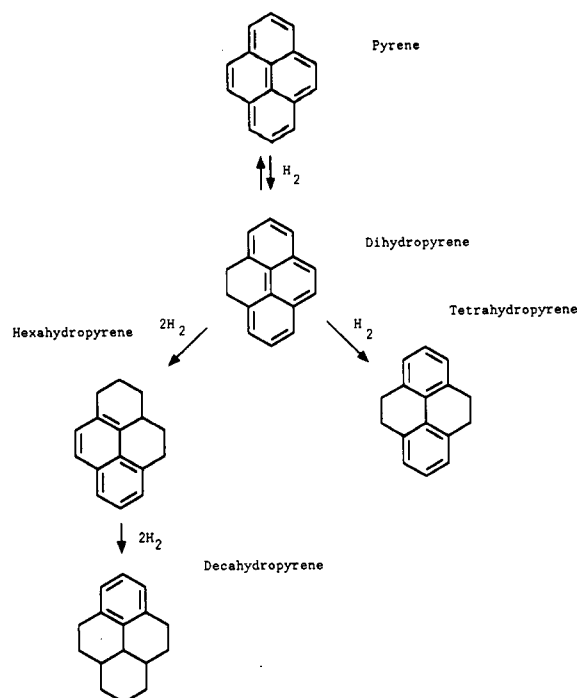(14) Veluswamy, L. R. Ph.D. Thesis, University of Utah, 1977.

Results and Discussion

The objective of this research was to evaluate the reactions and interactions among polynuclear aromatics, naphthenes, and other hydroaromatic and heteroatomic species in a catalytic reaction system employing oil-soluble molybdenum naphthenate (MoNaph) and sulfur that formed finely divided MoS₂ at coprocessing reaction conditions.[6] This objective was fulfilled by reacting pyrene (PY) in combination with other species at coprocessing conditions and evaluating their reaction products. The catalytic hydrogenation of PY was substantially inhibited by the presence of basic nitrogen. This result led to a study of the kinetics of PY hydrogenation in the presence of quinoline. The reaction products from the model reactants were determined individually but for ease of comparison among the different reactions the following terms were defined: percent hydrogenation (% HYD), percent hydrodesulfurization (% HDS), percent hydrodenitrogenation (% HDN), and percent hydrodeoxygenation (% HDO). Percent HYD is the number of moles of hydrogen required to achieve the final liquid product distribution as a percentage of the moles of hydrogen required to achieve the most hydrogenated product. Percent HDS, HDN, and HDO are the mole percents of liquid products not containing sulfur, nitrogen, and oxygen, respectively.

Pyrene Hydrogenation. PY, catalytically hydrogenated at 400 °C in hydrogen, produced a multiplicity of reaction products, including dihydropyrene (DHP), tetrahydropyrene (THP), two isomers of hexahydropyrene (HHP), and decahydropyrene (DCHP). A reaction pathway for PY hydrogenation in the presence of in situ sulfided MoNaph is postulated in Figure 1 on the basis of the reaction products observed as well as on the pathways presented in the literature.[8,12,14] DHP was readily formed and then either further hydrogenated to HHP or THP. The primary reaction pathway was through HHP based on the quantity of HHP formed, while the one to THP was secondary. THP was the terminal product in the secondary reaction pathway and present only in a small yield. The preference for hydrogenation of DHP to HHP rather than to THP possibly resulted from a difference in their respective aromatic saturation equilibrium. At these reaction conditions, the stereochemistry of the two molecules was also quite different. HHP contains two nonstrained hydroaromatic rings in a skewed chair structure that tends to be more resistant to dehydrogenation (DHY) than THP which contains two strained hydroaromatic rings.[8,12,14] No

Figure 1. Reaction pathway for pyrene hydrogenation under catalytic coprocessing conditions.

PY reacted in the absence of catalyst under these same conditions.

The results of catalytic hydrogenation reactions using PY with an additional model in the presence of in situ generated MoS_2 are given in Table I. The product distributions for the model components added in the reactions are given in Table II. The added models were perhydropyrene (PHP), amylcyclohexane (ACH), phenylundecane (PHU), tetralin (TET), dibenzothiophene (DBT), dibenzofuran (DBF), and quinoline (QUI). At 400 °C, PY conversion without an additional compound was about 92% with HHP as the primary product with DCHP as the most hydrogenated product. The addition of PHP, ACH, or PHU did not influence the product distribution obtained from PY. These compounds did not react and, hence, are not included in either Table I or II. When PY was catalytically reacted individually with TET, DBT, or DBF, the conversion of PY was about 90% at 400 °C yielding two isomers of HHP as the major products and DCHP as the most hydrogenated liquid product. With the addition of QUI to PY, PY conversion decreased to nearly 72% and the amount of hydrogenation of the products was substantially reduced. DHP was the primary reaction product.

At 425 °C PY conversion without an additional species present was approximately 69% and the major products were HHP and DHP. Because of the exothermic nature of the PY hydrogenation reaction, the equilibrium shifted toward the aromatic species;[12] hence, the conversion of PY decreased at higher reaction temperature. The addition of TET, DBF, and DBT to the reaction had little effect on PY conversion and reactivity. When PY and QUI were reacted together, the conversion of PY was only slightly lower at 68%. The PY product distributions for all of the reactions at 425 °C were very similar. Likewise, the product slates from PY reactions with QUI were similar at both temperatures.

At these conditions, hydrogenation was the only observed reaction of PY. The % HYD was determined for each reaction as presented in Table I. When PY was reacted in the presence of TET, DBF, or DBT at 400 °C,

Table II. Catalytic Hydrogenation of Tetralin and Heteroatomic Species in the Presence of Pyrene and in Situ Generated MoS₂

	reaction temperature	
	400 °C	425 °C
Product Distribution, mol %		
tetralin*[a]	94.8	92.2 ± 0.1
decalin	3.4	4.0 ± 0.4
naphthalene	1.8	3.8 ± 0.3
% HYD[b,g]	3.4	4.0 ± 0.4
% DHY[c]	1.8	3.8 ± 0.3
dibenzothiophene*	19.2 ± 1.6	6.8 ± 0.5
biphenyl	38.4 ± 1.1	53.1 ± 0.4
cyclohexylbenzene	39.4 ± 1.8	38.0 ± 0.2
bicyclohexyl	3.0 ± 0.8	2.1 ± 0.0
% HDS[d]	80.8 ± 1.6	93.2 ± 0.5
% HYD[g]	37.2 ± 1.7	39.1 ± 0.2
dibenzofuran*	93.7 ± 0.3	92.4 ± 0.6
cyclohexylbenzene	4.4 ± 0.2	6.0 ± 0.4
bicyclohexyl	1.9 ± 0.1	1.6 ± 0.2
% HDO[e]	6.3 ± 0.3	7.6 ± 0.6
% HYD[g]	4.6 ± 0.2	5.4 ± 0.4
quinoline*	0	0
tetrahydroquinoline	2.6 ± 0.5	0
propylaniline	10.9 ± 0.6	0
propylcyclohexene no. 2	4.5 ± 0.1	0
propylcyclohexene no. 1	6.5 ± 0.2	0
n-propylbenzene	14.1 ± 0.6	7.6 ± 0.1
n-propylcyclohexane	61.4 ± 1.7	92.4 ± 0.1
% HDN[f]	86.5 ± 0.5	100
% HYD[g]	84.2 ± 1.1	96.7 ± 0.1

[a] *Indicates the reactant. [b] HYD = hydrogenation. [c] DHY = dehydrogenation. [d] HDS = hydrodesulfurization. [e] HDO = hydrodeoxygenation. [f] HDN = hydrodenitrogenation. [g] For the calculation of percent hydrogenation, the most hydrogenated liquid product for: (1) tetralin was decalin, (2) dibenzothiophene was bicyclohexyl, (3) dibenzofuran was bicyclohexyl, (4) quinoline was n-propylcyclohexane.

38% HYD of PY was observed. The addition of QUI reduced the amount of PY HYD by half to only 17.9%. At 425 °C, the effect of QUI on PY hydrogenation was less significant than the effect of increased temperature. The combined reactions of PY with TET as well as DBF and DBT yielded about 22% HYD, while the presence of QUI had little effect, only reducing the % HYD to 21%. Thus, at the lower temperature of 400 °C the presence of QUI in the reaction caused substantial reduction of PY hydrogenation, but at the higher temperature, 425 °C, QUI had little influence on limiting PY hydrogenation.

Amylcyclohexane and 1-Phenylundecane Reaction. Neither ACH nor PHU reacted at either 400 or 425 °C. No dealkylation or hydrogenolysis occurred. The long aliphatic side chain on both the cyclohexyl and phenyl rings remained impervious to reaction or attack at coprocessing conditions in the presence of the finely divided MoS_2 catalyst. The phenyl ring in PHU did not undergo hydrogenation. Both species were stable and nearly 100% recoverable.

Tetralin Hydrogenation. TET underwent disproportionation when reacted in the presence of in situ generated MoS_2 and PY at both 400 and 425 °C. As given in Table II, TET showed low reactivity, with less than 10% conversion at both temperatures. At 400 °C, the amount of DEC was greater than that of NAP (3.4% versus 1.8%), indicating net hydrogenation of the TET. At 425 °C, the yields of DEC and NAP were equal. Higher reaction temperature favored the dehydrogenation of TET to NAP, thereby releasing hydrogen and donating it to the system. Frye[13] determined the equilibrium concentration of DEC, TET, and NAP at different hydrogen pressures and found that higher temperature favored the production of the

aromatic NAP as was observed in these reactions.

Dibenzothiophene Hydrodesulfurization. The catalytic hydrogenation of DBT with finely divided MoS$_2$ yielded biphenyl (BPH) as the primary product, cyclohexylbenzene (CHB) as the secondary product and bicyclohexyl (BCH) as a minor product (Table II). The % HYD of DBT ranged from 37 to 39% at both reaction temperatures. The amount of sulfur removal from DBT increased from about 80% HDS to more than 90% HDS when the reaction temperature was increased from 400 to 425 °C. Hence, at higher reaction temperatures desulfurization of DBT was favored over hydrogenation. Since the products obtained from this reaction kept the the aromatic rings intact, sulfur was removed from DBT without hydrogenolyzing and, often, without saturating the aromatic ring structure, thereby consuming less hydrogen than those heteroaromatic removal reactions requiring total ring saturation and hydrogenolysis.

Dibenzofuran Hydrodeoxygenation. The only two liquid products that could be detected from the catalytic hydrogenation of DBF were cyclohexylbenzene (CHB) and bicyclohexyl (BCH) (Table II). Only small amounts of both of these products were produced. Cyclohexylphenol has been suggested to be a reactive intermediate in oxygen removal from DBF, although it was not detected as a product in these reactions.[16] The % HDO of DBF was 6.3% at 400 °C and increased to 7.6% at 425 °C while the % HYD of DBF was 4.6% at 400 °C and 5.4% at 425 °C. Less than 10% conversion of DBF was observed at either temperature. These results showed the difficulty of hydrogenating or removing the oxygen from a multiring structure using the finely divided MoS$_2$. Other researchers have shown the need for ring saturation prior to oxygen removal from multiring systems.[15,16] Since only a small amount of deoxygenation occurred, finely divided MoS$_2$ was not particularly active for oxygen removal from multiring aromatic compounds, although it has been shown to be active for removing hydroxyl groups from phenols and oxygen from benzofuran.[10]

Quinoline Hydrodenitrogenation. The reaction of QUI with finely divided MoS$_2$ at 425 °C, resulted in total conversion and complete hydrodenitrogenation of QUI and production in n-propylcyclohexane (PCH) as the primary product at 92%. The minor product was also a hydrocarbon, n-propylbenzene (PB) at 8%. At 400 °C, QUI was again converted totally with about 86% HDN occurring. The only nitrogen-containing products observed were o-propylaniline (OPA) at nearly 11% and 1,2,3,4-tetrahydroquinoline (THQ) at less than 3%. Hence, denitrogenation of QUI was promoted at the higher temperature. Ring saturation, required for nitrogen removal, was effectively, promoted by the presence of in situ generated the MoS$_2$ catalyst. This denitrogenation of QUI is consistent with that reported by Kim and Curtis[10,11] using MoNaph and excess sulfur and by Satterfield et al.[17] using NiMo/Al$_2$O$_3$.

Comparison of Heteroatom Removal. HDO and HDN at coprocessing conditions have been shown to be more difficult than HDS[10,11,18,19] and require more severe conditions and a more active catalyst. The differences in the propensity of the different heteroatom removal reac-

(15) Hall, C. C.; Cawley, C. M. *J. Soc. Chem. Med.* **1939**, *58*, 7.
(16) Badilla-Ohlbaum, R.; Pratt, K. C.; Trimm, D. L. *Fuel* **1979**, *58*, 309–314.
(17) Satterfield, C. N.; Smith, C. M. *Ind. Eng. Chem. Process Des. Dev.* **1986**, *25*, 942–949.
(18) Rollmann, L. D. *J. Catal.* **1977**, *46*, 243–252.
(19) Katzer, J. R.; Sivasubramanian, R. *Catal. Rev. Sci. Eng.* **1979**, *20*, 155–160.

Table III. Bond Energies between Carbon and Heteroatoms in Polyatomic Molecules[a]

bond	energy, kcal/mol	bond	energy, kcal/mol
C–H	99	C–N	73
C–C	83	C=N	147
C=C	146	C–S	65
N–H	93	C=S	128
S–H	83	C–O	86
O–H	111	C=O	176

[a] Reference 21.

tions and the need to saturate aromatic ring systems prior to carbon–oxygen or carbon–nitrogen scission can be partially explained by comparing the C–C, C–O, C–S, and C–N bond strengths for single and double bonds as shown in Table III. C–O and C–N bonds always have a higher bonding energy in their respective single- and double-bond systems than do C–S bonds. C–O and C–N double bonds have slightly greater bond strength than do C–C double bonds.[19]

Kinetics of Pyrene and Quinoline Catalytic Hydrogenation Reactions

Combined Pyrene and Quinoline Reactions. Catalytic reactions of PY combined with different weight percentages of QUI were performed at 400 °C using finely divided MoS$_2$ as shown in Table IV. The amount of PY HYD occurring based on the hydrogenated products formed was determined at each QUI concentration level. Likewise, the amount of QUI HYD and HDN was also determined.

The yield of the hydrogenated PY products decreased as QUI concentration increased. PY conversion was 90% when the QUI concentration was less than 0.5 wt %. HHP isomers were the primary products, DHP was the secondary product, and DCHP was present at the least concentration. As the QUI concentration increased, the amount of PY conversion decreased as did the extent of hydrogenation of the products. For example, when the QUI concentration was increased to 1 wt %, more than 70% of the PY was converted but only a trace amount of DCHP was detected. DHP was the primary product and HHP was the secondary product. When the QUI concentration was increased further from 1 to 4 wt %, PY conversion decreased from 70 to 56%, yielding DHP and lesser amounts of HHP and THP as products. At 10 wt % quinoline concentration, PY conversion was decreased further to about 45% with DHP as the major product, THP as a minor product, and only a trace amount of HHP being formed.

Examination of the QUI reactivity given in Table V shows that QUI completely converted within 30 min of reaction of all weight addition levels. At a QUI concentration of less than 0.5 wt %, PCH was the only product observed, indicating 100% HYD and HDN of QUI. As the QUI concentration was increased, the amount of HYD and HDN decreased. For example, when the QUI concentration was increased from 1 to 2 wt %, nitrogen-containing secondary products, including THQ and OPA, were produced as well. At a QUI concentration of 10 wt %, THQ was the primary product present at a range between 70 and 80%, while the yield of hydrocarbons was less than 18%.

The inhibition of PY HYD by increased QUI concentration is demonstrated in Figure 2. When the % PY HYD is plotted against QUI concentration, a significant decrease of PY HYD from 38 to 19% occurred as the QUI concentration increased from 0.0 to 2.0 wt %. This in-

Table IV. Catalytic Hydrogenation of Pyrene and Quinoline with in Situ Generated MoS_2[a]

weight percent quinoline	product distribution from pyrene, mol %								
							unknown		
	PY[b]	DHP	THP	HHP	HHP*	DCHP	1	2	% HYD[c]
0.31	7.6	11.0	4.4	27.2	20.1	9.3	8.3	12.1	38.8
0.45	9.6	13.5	trace	28.6	20.1	8.9	7.6	11.7	37.6
0.55	11.2	15.6	4.5	25.0	16.1	11.6	7.9	8.1	35.7
1.09	29.3	35.9	11.1	15.6	8.1	trace	trace	trace	16.2
1.10	26.8	32.0	9.5	16.6	9.9	2.1	3.1	trace	19.4
2.12	36.9	37.8	9.9	5.8	9.6	0	0	0	13.0
2.24	36.5	36.8	10.5	9.4	6.8	0	0	0	13.3
3.97	39.4	41.9	8.0	6.1	4.6	0	0	0	11.2
4.14	43.9	41.4	trace	6.1	8.6	0	0	0	10.7
10.01	57.1	35.2	4.1	3.6	trace	0	0	0	6.8
10.01	52.4	42.2	5.4	trace	trace	0	0	0	6.6
10.02	54.0	40.1	5.9	trace	trace	0	0	0	6.5

[a] Reaction conditions: 400 °C, 30 min, 1500 ppm Mo as molybdenum naphthenate, and 4 g loading of 1 wt % pyrene in hexadecane. [b] PY (pyrene), DHP (dihydropyrene), THP (tetrahydropyrene), HHP (hexahydropyrene), HHP* (another isomer of HHP), DCHP (decahydropyrene), unknown 1 and 2 (most probably isomers of DCHP). [c] For the calculation of percent hydrogenation, perhydropyrene was used as the most hydrogenated liquid product.
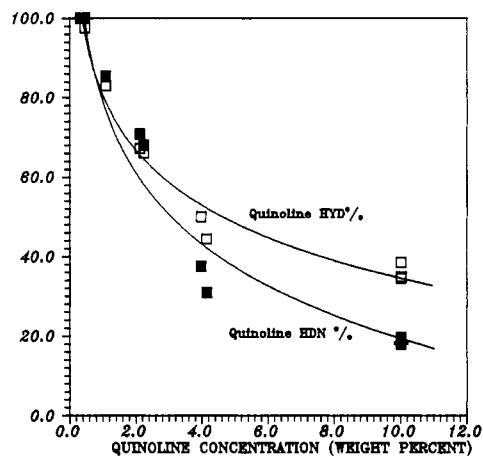
Table V. Catalytic Hydrogenation of Pyrene and Different Weight Percents of Quinoline with in Situ Generated MoS_2[a]

weight percent quinoline	product distribution from quinoline, mol %						% HYD[c]	% HDN
	THQ[b]	OPA	PB	PCHxe 1	PCHxe 2	PCH		
0.31	0	0	0	0	0	100	100	100
0.45	0	0	0	0	0	100	100	100
0.47	0	0	4.1	4.4	trace	91.5	97.6	100
1.09	3.1	11.5	14.7	6.6	4.4	59.7	83.0	85.4
2.12	29.2	trace	23.4	9.4	4.7	33.3	67.2	70.8
2.24	32.0	trace	22.9	9.1	trace	36.0	66.0	68.0
3.97	61.0	trace	13.9	5.4	5.3	14.4	48.9	38.5
4.14	69.2	trace	11.9	4.8	2.8	11.3	44.4	30.8
10.01	73.6	8.5	7.7	3.0	1.9	5.3	38.5	17.9
10.01	80.5	9.3	4.3	1.8	1.0	3.1	34.9	19.5
10.02	81.6	9.1	4.0	1.6	0.9	2.8	34.5	18.4

[a] Reaction conditions: 400 °C, 30 min, 1500 ppm Mo as molybdenum naphthenate, and 4 g loading of 1 wt % pyrene in hexadecane. [b] THQ (tetrahydroquinoline), OPA (o-propylaniline), PB (propylbenzene), PCHxe (propylclohexene), PCH (propylcyclohexane). [c] For the calculation of hydrogenation, n-propylcyclohexane was used as the most hydrogenated liquid product.
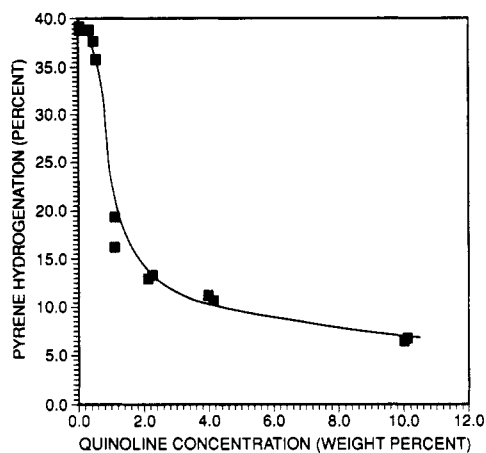
Figure 2. Catalytic hydrogenation of pyrene in the presence of different concentrations of quinoline and in situ generated MoS_2.

Figure 3. Hydrogenation and hydrodenitrogenation of quinoline in the presence of pyrene and in situ generated MoS_2.

hibition was most likely caused by the poisoning of the MoS_2 catalyst surface by QUI and the nitrogen-containing products as they were formed and adsorbed on the catalyst surface. These secondary products were probably stronger poisons since the basicity of nitrogen compounds increases with the degree of hydrogenation.[20] The change in basicity as implied here is only relative and determined by the degree of interaction with relatively weak acids.[20] These

secondary nitrogen products have been shown to be more resistant to nitrogen removal than the original reactant QUI and cannot only inhibit further HYD of PY hydrogenated products but also themselves.[19,20] The % HYD and % HDN of QUI are presented in Figure 3 and show decreased catalytic activity for the HYD and HDN of QUI as the amount of QUI in the system increased.

Kinetics of Pyrene and Quinoline Hydrogenation. The kinetics of the catalytic HYD reactions of PY and QUI at low and high QUI concentrations were evaluated by determining the reaction products at different reaction times. The product distribution of PY HYD in the presence of 10 wt % QUI and of finely divided MoS_2 is

(20) Larson, O. A. *Prepr. Pap.—Am. Chem. Soc., Div. Pet. Chem.* **1967,** *12*(4), 13–15.

(21) Roberts, J. D.; Stewart, R.; Caserio, M. C. *Organic Chemistry*; Benjamin: Menlo Park, CA, 1971.

Table VI. Quinoline Product Distribution from Reactions with Pyrene and in Situ Generated MoS₂ at Varying Times[a]

reaction time, min	product distribution from quinoline, mol %						% HYD[c]	% HDN
	THQ[b]	OPA	PB	PCHxe 1	PCHxe 2	PCH		
10 wt % QUI								
5	98.2 ± 0.1	1.8 ± 0.1	0	0	0	0	28.8 ± 0	0
10	96.0 ± 0.4	4.0 ± 0.4	0	0	0	0	29.2 ± 0.1	0
30	79.7 ± 2.3	8.6 ± 1.1	4.9 ± 1.4	2.0 ± 0.6	1.3 ± 0.5	3.5 ± 0.9	35.6 ± 1.5	11.7 ± 3.4
50	74.0 ± 2.0	9.8 ± 3.1	6.9 ± 0.8	2.7 ± 0.4	1.7 ± 0.2	4.9 ± 0.4	37.9 ± 0.5	16.2 ± 1.8
0.4 wt % QUI								
2.5	84.9 ± 1.5	1.9 ± 0.1	7.3 ± 2.8	0	0	5.9 ± 0.7	35.2 ± 1.0	13.2 ± 3.5
5	0	0	41.1 ± 0.4	17.0 ± 1.4	7.5 ± 2.5	34.4 ± 0.8	78.9 ± 0	100
10	0	0	35.8 ± 1.2	13.8 ± 1.8	6.3 ± 1.2	44.1 ± 2.1	81.9 ± 0.7	100
30	0	0	2.0 ± 0.2	2.2 ± 0.2	0	95.8 ± 4.2	98.8 ± 1.2	100
50	0	0	0.3 ± 0.2	2.8 ± 0.2	0	96.9 ± 3.1	99.6 ± 0.4	100

[a] Reaction conditions: 400 °C, 30 min, 1500 ppm Mo as molybdenum naphthenate, and 4 g loading of 1 wt % pyrene and 0.4 or 10 wt % quinoline in hexadecane. [b] THQ (tetrahydroquinoline), OPA (o-propylaniline), PB (propylbenzene), PCHxe (propylcyclohexene), PCH (propylcyclohexane), QUI (quinoline). [c] For the calculation of percent hydrogenation, n-propylcyclohexane was used as the most hydrogenated liquid product.
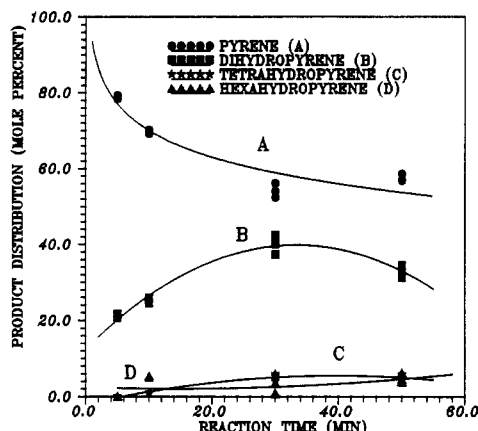

Figure 4. Product distribution from the catalytic hydrogenation of pyrene in the presence of 10 wt % quinoline and in situ generated MoS₂.

Figure 5. Product distribution from the catalytic hydrogenation of pyrene in the presence of 0.4 wt % quinoline and in situ generated MoS₂.

presented in Figure 4. The most highly hydrogenated PY products observed were isomers of HHP which were present at trace levels. DHP was the predominant product and its formation reached a maximum of 40% after 30 min. These results indicate that the catalyst was poisoned by the 10 wt % QUI and had only an activity level sufficient to convert 40% of the PY.

In this same reaction, the rate of QUI conversion to THQ was very rapid so that within 5 min all QUI was converted as shown in Table VI. After 10 min, the nitrogen-containing products OPA and THQ were observed but no denitrogenation had occurred. After 30 min of reaction the products consisted of OPA, THQ, and 10% hydrocarbons that were principally PCH and PB. After 50 min of reaction, somewhat less THQ was present and slightly more hydrocarbons were formed. The high concentration of QUI and its reaction products strongly inhibited the rates of their own hydrogenation and denitrogenation reactions, which most likely occurred because of their strong competitive adsorption on catalyst surfaces.[19,20] Because of the self-inhibiting effect of QUI on HDN, severe operating conditions or higher catalyst loading would be required to achieve the nitrogen removal in systems with a high organic nitrogen content.

The HYD of PY in the presence of 0.4 wt % QUI given in Figure 5 shows a maximum peak for DHP formation when the reaction time approached 10 min. At a reaction time of greater than 10 min, nearly 60% PY was converted to DHP as the primary product and to isomers of HHP as secondary products. When the reaction time reached 50 min, PY conversion increased to approximately 90%,
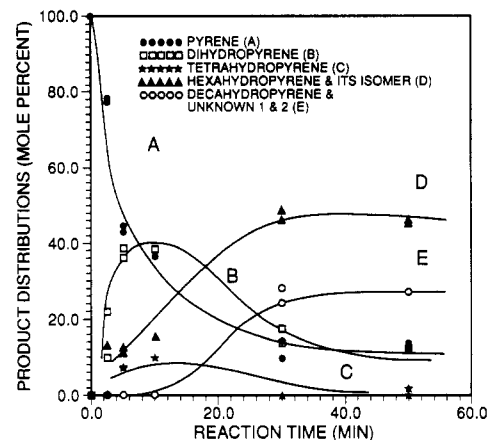
yielding isomers of HHP as the primary products and DCHP as the most hydrogenated liquid product. The % HYD after 50 min was about 35%. A 4-h reaction was also performed to determine if the system was approaching equilibrium. PY conversion increased slightly and small increases in the hydrogenated products were observed compared to the 50-min reaction. The % HYD rose to 39%. At the 0.4 wt % loading, QUI completely denitrogenated within 5 min and converted to hydrocarbon products of PCH and PB as presented in Table VI. Further HYD of QUI and it reaction products occurred after 30 min yielding PCH as the only liquid product.

The % PY HYD and % QUI HYD that occurred at 0.4 and 10 wt % of QUI concentrations as a function of time are given in Figure 6. PY HYD approached 95% of its maximum value within 30 min at both quinoline concentrations. At high QUI concentration, PY HYD was below 10% even after 50 min of reaction. At low QUI concentration, PY HYD was more than 10% within 10 min and increased to 35% as the reaction time increased to 50 min. By contrast, QUI HYD dramatically increased within the first 5–10 min of reaction at both high and low quinoline concentrations. QUI at the lower concentration level achieved 82% HYD within 10 min. Complete denitrogenation and nearly total hydrogenation of QUI occurred within 30 min of reaction. At high QUI concentration, 29% QUI HYD was achieved within 10 min and increased to 38% after 50 min.

Several researchers have focused on the first stages of the pyrene–hydropyrene reaction mechanism at reaction times up to 30 min. The formation and reaction of DHP
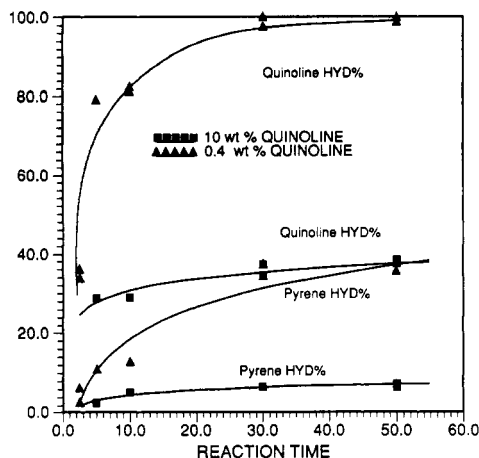
Figure 6. Pyrene and quinoline hydrogenation at two concentration levels of quinoline in the presence of in situ generated MoS_2.

Figure 7. Irreversible kinetics for hydrogenation of pyrene in the presence of 0.4 and 10 wt % quinoline and in situ MoS_2.

were important for hydrogen transfer in the PY systems.[7,8,12] Stephens and Kottenstette defined a pseudo-first-order reaction network for PY hydrogenation at 548–673 °C and 3.4–13.8 MPa of hydrogen, based on batch kinetic data using Shell 324 catalyst.[7] PY was reacted in hexadecane and in hydrogenated Koppers creosote oil. The results from these reactions indicated that the hydrogenation of PY was reversible and thermodynamically limited at high reaction temperatures. The formation of hydrogenated PY products was favored kinetically at low reaction temperature. Johnston also used pseudo-first-order kinetics to describe PY hydrogenation and dehydrogenation under catalytic conditions at 648 K and 7.2 MPa using presulfided $CoMo/Al_2O_3$ catalyst.[8] On the basis of this work, Johnston considered that the equilibrium constant for catalytic PY hydrogenation may be more important than the hydrogenation rate constant because of the rapid equilibration that occurred between PY and DHP.

A kinetic approach similar to the pseudo first order given in the literature[7,8] was used in this study. The integrated expression obtained for a first-order irreversible kinetic reaction was applied for the conversion of PY in the catalytic hydrogenation reactions containing 0.4 and 10 wt % QUI in the individual systems. The respective rate constants for the two nitrogen levels reactions were obtained by plotting ln (C_{PYO}/C_{PY}) versus reaction time as shown in Figure 7. The parameters in the figure are defined as C_{PYO}, the initial PY concentration, C_{PY}, the final PY concentration; K_1 and K_2 are the rate constants for the low and high QUI concentrations, respectively. The kinetic data on Figure 7 show that the rate constant of the conversion of PY decreased from 0.0426 to 0.0089 min^{-1} as the initial QUI concentration increased from 0.4 to 10 wt %. Because there was no further PY conversion as the reaction time was increased from 30 to 50 min for the QUI-PY system, a plot of ln (C_{PYO}/C_{PY}) versus reaction time up to 30 min is also presented in Figure 7. Reevaluation of the rate constants, K_1 and K_2, gave increased rate constants of 0.0733 and 0.0198 min^{-1}, respectively, at the shorter reaction time. Thus, PY HYD occurred much more rapidly at low nitrogen levels in the presence of the in situ generated MoS_2 catalyst.

Summary and Conclusions

The hydrogenation of pyrene under coprocessing conditions using finely divided MoS_2 catalyst was not affected by the addition of hydrocarbon or heteroatomic species containing sulfur and oxygen but was poisoned substan-
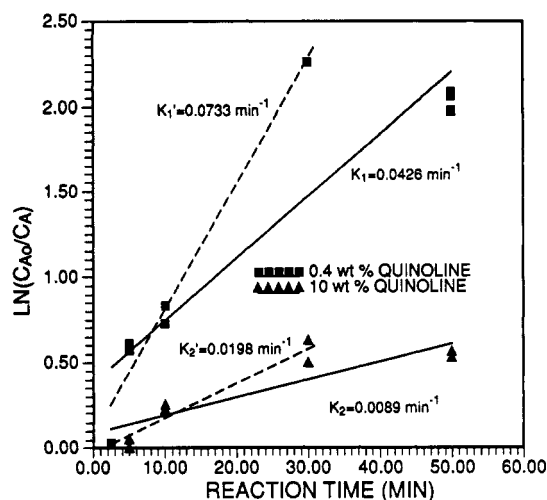
tially by quinoline containing nitrogen at 400 °C. At 425 °C, thermodynamics limited pyrene hydrogenation to half the amount occurring at 400 °C. None of the added compounds had any effect on pyrene hydrogenation. The added components varied in reactivity. The hydrocarbons showed little if any reactivity. No hydrocracking occurred. The reactions of the heteroatomic species ranged from little hydrogenation or oxygen removal for dibenzofuran to substantial hydrogenation and sulfur removal for dibenzothiophene, to nearly complete hydrogenation and nitrogen removal for quinoline. The degree of quinoline reactivity was dependent upon the amount of quinoline present and the temperature of the reaction.

The kinetics of pyrene and quinoline hydrogenation with finely divided MoS_2 showed that the hydrogenation of pyrene was inhibited when the quinoline concentration was increased from 0.4 to 10 wt %. At high concentration, quinoline required longer reaction times to achieve the same extent of nitrogen removal as the reactions with lower nitrogen concentration. Pyrene hydrogenation was not affected by the low concentration of 0.4 wt % of quinoline. However, the kinetics of pyrene hydrogenation were substantially affected by the high weight percent of quinoline. The reactions in the tubular bomb reactors only required 50 min to achieve a pseudoequilibrium state. Longer reaction times resulted in little additional reaction for either pyrene or quinoline.

Nomenclature

ACH = amylcyclohexane
BCH = bicyclohexyl
BPH = biphenyl
CHB = cyclohexylbenzene
DBF = dibenzofuran
DBT = dibenzothiophene
DCHP = decahydropyrene
DEC = decalin
DHP = dihydropyrene
DHY = dehydrogenation
HDN = hydrodenitrogenation
HDO = hydrodeoxygenation
HDS = hydrodesulfurization
HHP = hexahydropyrene
HYD = hydrogenation
NAP = naphthalene
OPA = o-propylaniline
PB = propylbenzene

PCH = propylcyclohexane
PCHxe = propylcyclohexene
PHU = 1-phenylundecane
PY = pyrene
PHP = perhydropyrene
QUI = quinoline
TET = tetralin
THP = tetrahydropyrene

THQ = tetrahydroquinoline

Registry No. S, 7704-34-9; MoS$_2$, 1317-33-5; pyrene, 129-00-0; dibenzofuran, 132-64-9; dibenzothiophene, 132-65-0; quinoline, 91-22-5; tetralin, 119-64-2; amylcyclohexane, 4292-92-6; 1-phenylundecane, 6742-54-7; dihydropyrene, 28779-32-0; tetrahydropyrene, 66161-17-9; hexahydropyrene, 20330-24-9; decahydropyrene, 55101-66-1; perhydropyrene, 2435-85-0.

Semiquantitative FTIR Analysis of a Coal Tar Pitch and Its Extracts and Residues in Several Organic Solvents

M. D. Guillén,[*,†] M. J. Iglesias,[‡] A. Domínguez,[‡] and C. G. Blanco[‡]

Instituto Nacional del Carbón, C.S.I.C., Ap. 73, 33080 Oviedo, Spain, and Facultad de Farmacia, UPV, Portal de Lasarte s/n, 01007 Vitoria, Spain

The infrared spectra from 650 to 4000 cm^{-1} and their semiquantitative analysis for a coal tar pitch and extracts and residues obtained when this coal tar pitch was treated with organic solvents are discussed. This analysis supplies excellent information on the concentration of the several functionalities in the samples. The treatment with solvents provides carbonaceous materials with different concentrations of the same functionalities which can be very useful in the study of relationships between composition, properties, and behavior. The different aromaticity of the samples, in relation with the hydrogen, are discussed. A preponderance of aromatic hydrogens, distributed mainly in structures containing four neighboring aromatic C–H bonds, and an appreciable amount of hydrogens attached to saturated carbon atoms, even in the insoluble fractions, can be observed. In general, the solvent's ability to extract these two kinds of C–H bond is proportional to the solvent's effectiveness and the porportionality constant is a function of the concentration of these functional groups in the coal tar pitch. Furthermore, the existence of structures containing carbonyl groups in the coal tar pitch and its fractions, which cannot be detected by other techniques, have been observed. Finally, it was found that solvents like methanol and ethanol provide extracts very rich in carbazole derivatives, but certain solvents are able to extract a higher amount of these derivatives.

Introduction

Coal tar pitches have very important industrial applications. For this reason an effective characterization is required. But this characterization is difficult because of the very large number of constituent compounds. Another serious difficulty results from the fact that many of the empirical pitch properties have no connection with molecular structural features.

An adequate approach in the characterization of coal tar pitches may be sample fractionations[1-3] and subsequent analysis of the fractions obtained. Thus, in our continuing interest to explain pitch behavior, the effectiveness of a number of organic solvents in the extraction of coal tar pitches[4] and relationships between this effectiveness and the solvent solubility parameters[5,6] have been reported.

Another possible approach is the characterization of the volatile fraction by searching for a connection between this fraction and the properties of the coal tar pitch as a whole. Therefore, the components of the volatile fraction of a coal tar pitch were analyzed.[7,8] However, these volatile compounds are a small part of the coal tar pitch, and therefore it could be of widespread interest to make a quantitative study not only of the volatile fraction by means of capillary gas chromatography[9] but also of the whole material using other analytical techniques such as Fourier transform infrared spectroscopy (FTIR).

Despite the very large number of papers on quantitative measures by IR spectroscopy in coals,[10,11] in most of the

Table I. Extraction Yields of A1 Coal Tar Pitch Obtained with Several Solvents[a]

no.	solvent	yield, %
1	hexane	14.0
2	methanol	14.1
3	ethanol	28.2
4	acetone	49.0
5	carbon tetrachloride	50.8
6	toluene	59.6
7	chloroform	65.8
8	carbon disulfide	66.7
9	tetrahydrofuran	69.7
10	pyridine	72.2

[a] Reference 4.

(1) Blümer, G.-P.; Kleffner, H. W.; Lücke, W.; Zander, M. *Fuel* 1980, 59, 600.
(2) Boenigk, W.; Haenel, M. W.; Zander, M. *Fuel* 1990, 69, 1226.
(3) Bartle, K. D. *Rev. Pure Appl. Chem.* 1972, 22, 79.
(4) Guillén, M. D.; Blanco, J.; Canga, J. S.; Blanco, C. G. *Energy Fuels* 1991, 5, 188.
(5) Blanco, C. G.; Guillén, M. E. *Ind. Eng. Chem. Res.* 1991, 30, 1579.
(6) Blanco, C. G.; Guillén, M. D. *Fuel* 1992, 71, 295.
(7) Blanco, C. G.; Blanco, J.; Bernad, P.; Guillén, M. D. *J. Chromatogr.* 1991, 539, 157.
(8) Guillén, M. D.; Iglesias, M. J.; Domínguez, A.; Blanco, C. G. *J. Chromatogr.* 1992, 591, 287.
(9) Guillén, M. D.; Domínguez, A.; Iglesias, M. J.; Blanco, C. G. *J. Chromatogr.*, in press.

†Facultad de Farmacia, UPV.
‡Instituto Nacional del Carbon.