

## KINETICS OF HEAVY OIL/COAL COPROCESSING

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### INTRODUCTION

A number of studies have been reported on coprocessing of coal and oil sand bitumen, petroleum residues and distillate fractions in catalytic and non-catalytic processes (Moschopedis et al., 1984ab, Ignasiak et al., 1984, Kelly et al., 1984, Fouda et al., 1982, MacAurthur et al., 1985, Curtis et al., 1984). The studies described the effects of feedstock characteristics, process chemistry and operating variables on the product yield and distribution; however, very few kinetic data were reported in these investigations. This paper presents the kinetic data and modelling of the CANMET coal/heavy oil coprocessing process.

CANMET has been conducting research and process development work on coprocessing of Canadian heavy oil/bitumen and coal since 1979 including studies of the kinetics and mechanisms of coprocessing. As a continuation of the program, CANMET and Lobbe Technologies undertook a project on mathematical modelling of coprocessing kinetics with emphasis on the development of reaction engineering models for improved process performance and operation. The results of that project were reported in much detail elsewhere (Szladow et al., 1987).

### EXPERIMENTAL

The coprocessing experiments were conducted in a continuous-flow stirred-tank coprocessing reactor unit. A detailed description of this unit was given by Fouda et al. (1982). The applied reactor equations were those for CSTR, based on conclusions from the exploratory runs which investigated the effect of impeller speed on the yield of reaction products.

Alberta subbituminous coal and Cold Lake, Alberta, vacuum bottoms (+454°C) were used as the feedstock. The coal was ground to -200 mesh and slurried with heavy vacuum bottoms by mixing about 30 percent of coal and 70 percent of heavy oil (d.a.f. slurry basis). A disposable iron sulphide catalyst was added in the amount of approximately 5 percent on a d.a.f. slurry basis.

The experimental conditions were designed using a Latin Square statistical design at three levels of temperature and space velocity. The range of process conditions included:

Temperature: 400 to 455°C  
 Nominal Slurry Space Velocity: 0.50 to 1.54 kg/L/hr  
 Reactor Pressure: 2000 psig  
 Run Duration: 80 to 180 min.  
 Total Feed Processed: 402 to 600g  
 Coal Concentration: 29.71 to 33.38 m.a.f. Wt% feed

The coprocessing products were analyzed for four liquid fractions, solvent soluble and insoluble fractions, gaseous products, hydrogen consumption, and coal and pitch conversion. Distillate products were also analyzed for composition and specific gravity. The residue (+525°C) was analyzed for elemented composition and ash content. A summary of the product definitions and separation procedures is depicted in Figure 1. The percent recovery of the input feed was between 96.40 and 105.02 percent with the mean of 100.78 and standard deviation of 2.84 percent. These accurate mass balances for the product yield facilitated high predictive capabilities of the developed models.

Two different types of models were formulated for predicting the yield structure of coprocessing products: 1) models which had sequential characteristics; and 2) models with parallel characteristics, where most coprocessing products were generated from the initial lumps (Figure 2). In the sequential models, the distillate products always reached a maximum beyond which addition of more hydrogen resulted in generation of C1-C4 hydrocarbon gases. In the parallel models, the yield of distillate products continuously increased - within the range of coprocessing conditions - and the selectivity of products was determined by the relative rates of their formation.

A set of generalized lumped kinetic model equations was derived for an n-component reacting mixture in a stirred-tank reactor:

$$\frac{F_{in} (1 - \phi)}{(1 - \epsilon) \rho_P V_R} (x_{i,0} - X_i) = r_i'$$

where  $F_{in}$  = rate of total feed input, kg/hr (d.a.f.)  
 $\phi$  = mass fraction of product flashed at reactor T,P  
 $\rho_P$  = average density of products, kg/L  
 $V_R$  = reactor volume (to the dip tube), L<sup>3</sup>  
 $\epsilon$  = gas holdup  
 $X_{i,0} = F_{i,in} / F_{in}$   
 $r_i' = F_{i,out} / F_{in}$   
 $r_i$  = rate of formation (disappearance) for component "i" in terms of fractional conversion,  $X_i$ , hr<sup>-1</sup>

The equations were solved using a Least Square method and the product yield structure for each coprocessing component. The computer algorithms first solved the normal equations developed for the rate parameters,  $k_{ij}$ , and later, solved for the rate constant coefficient  $A_{ij}$  and  $E_{ij}$ . This approach provided information on how the calculated rate constants,  $k_{ij}$ , change with the alternative reaction networks. The approach also permitted better understanding of the physical meaning underlying the regressed rate constants and the postulated product yield structures for coprocessing.

A number of studies have been published documenting the pitfalls of using lumped kinetic models for reacting mixtures, in general (Liu et al., 1973, Luss et al., 1971) and for coal liquefaction in particular (Szladow et al., 1981, Prasad et al., 1986). The most common pitfalls reported were the loss of information about the kinetics of individual reactions, different rate expressions for the grouped as opposed to individual species rate equations, little theoretical significance underlying the overall (lumped) activation energies, and the frequent discrepancy between the order of the rate expressions for lumps and for reacting species. Several investigators also showed methods which overcome these difficulties for complex reacting mixtures, (Golikeri et al., 1974, Lee, 1978, Bailey, 1972). These methods were later extended to coal liquefaction (Szladow et al., 1982, Prasad et al., 1986).

Bearing in mind the above limitations of lumped kinetics, the CANMET coprocessing data and product lumping were reviewed to establish whether the product lump definitions were dependent on the severity of the process. The analysis of variance which was performed indicated that product characteristics did not change with the severity of coprocessing reactions. Also, analysis of activation energies for THFI using methods reported by Szladow et al. (1981) showed that one initial lump is sufficient for expressing coal reactivity.

Over twenty different reaction networks were developed and tested based on ANOVA tables and Multiple Classification Analysis of the coprocessing products. A significant number of the networks predicted the coprocessing data structure and met the identified constraints on the rate coefficients. The selection of suitable models was based, therefore, on three criteria:

1. How much of the total variance was explained by the model.
2. How much of the grouped product's variance was explained by the model.
3. How well the model predicts the yields of coprocessing products or how accurate the model is.

First, criterion 1 was used, later, as specific difficulties were addressed, criteria 2 and 3 were reviewed. This approach allowed a systematic evaluation of the models, in conjunction with the interpretation of the rate constants and reaction paths.

Special difficulties were also experienced with modelling preasphaltenes. Figure 3 depicts the effect of temperature on the yield of preasphaltenes. As the temperature increased from 400 to 425°C the yield of preasphaltenes increased; however, the yield of preasphaltenes decreased as the temperature increased from 425 to 450°C, indicating a change in the sign of the temperature coefficient (activation energy). This led us to believe that two mechanisms may be responsible for preasphaltenes formation: one essentially being a chemical reaction mechanism of THFI conversion, with the rates increasing with temperature, and the second representing an adduct formation between preasphaltenes and oils, for which the rate decreases with temperature.

Cronauer et al. (1979) and Sato (1976) reported similar effects for coal liquefaction. They observed a net negative yield of oil at low

primary liquefaction products. Our analysis of the CANMET experiment revealed that other coals also exhibit similar "reverse" temperature effects at lower temperatures. At high temperatures, the adduct seemed to disintegrate.

To account for the two opposed mechanisms, one would have to postulate independent rate expressions for chemical reactions and for adduct formation of preasphaltenes. Considering, however, that preasphaltenes constitute only a small fraction of the overall coprocessing products (5 to 10 percent), we decided to retain the parallel structure for preasphaltenes reactions, with only one reaction path leading to its formation. This approach had resulted in somewhat inaccurate modelling of preasphaltenes, but it allowed modelling of the remaining coprocessing reactions.

The final choice of parallel and sequential models is presented in Figure 4. Model 52 has a strong parallel characteristic for the yield of distillate fractions with the prime coprocessing products (light gas oil, naphtha and hydrocarbon gas) constituting the termination lumps for the coprocessing network. Model 61 has sequential characteristics with the exception of the formation paths for the C1-C4 group.

The regressed rate constants for Model 52 and 61 are shown in Table 1. Both models predicted the coprocessing yield data accurately (Figures 5 and 6). The amount of variance explained by the models is shown in Table 2. Model 52 explains 84.4 percent of the total variance. For individual components the variance explained exceeds or is close to the target variance for preasphaltenes, asphaltenes, oils, naphtha and the C1-C4 group. Model 61 explained 81.4 percent of total variance and achieved target variance for THFI, asphaltenes and oils and was close for the C1-C4 group. Interestingly enough, when tested without path #8, Model 61 could not predict the C1-C4 yield accurately.

In the final step, Model 52 was improved by adding two more reaction paths to meet the limiting conditions, i.e., at infinite time distillate fractions should be converted to lighter products (Figure 7). Model 53 explained 90.0 percent of variance, which is very satisfactory, considering the difficulties with modelling preasphaltenes. Model 53 also explained most of the individual component variance except for light gas oil and naphtha.

#### **SUMMARY AND CONCLUSION**

A number of reaction networks were evaluated for CANMET coprocessing. The final choice of model was a parallel model with some sequential characteristics. The model explained 90.0 percent of the total variance, which was considered satisfactory in view of the difficulties of modelling preasphaltenes.

The models which were evaluated showed that the kinetic approach successfully applied to coal liquefaction and heavy oil upgrading can be also applied to coprocessing. The coal conversion networks and heavy oil upgrading networks are interrelated via the forward reaction paths of preasphaltenes, asphaltenes, and THFI and via the reverse kinetic paths of an adduct formation between preasphaltenes and heavy oil.

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**Table 1. RATE CONSTANT COEFFICIENTS  
FOR MODEL 52 , 61, AND 53**

Rate Constant	MODEL 52		MODEL 61		MODEL 53	
	<u>Ai</u>	<u>Ei</u>	<u>Ai</u>	<u>Ei</u>	<u>Ai</u>	<u>Ei</u>
1	1.24E10	33,020	5.33E13	44,040	1.24E10	33,020
2	8.31E23	76,180	5.23E03	12,030	9.11E23	77,730
3	1.84E12	39,030	8.33E08	29,390	1.84E12	39,030
4	1.72E12	40,000	9.48E18	61,030	1.51E12	40,000
5	4.97E17	58,910	5.56E09	31,990	4.17E17	59,610
6	4.06E19	63,400	7.90E06	23,310	4.06E19	63,400
7	7.90E06	23,510	6.53E02	13,860	7.90E06	23,510
8	2.28E14	47,470	1.50E06	55,000	2.28E14	47,470
9	-	-	-	-	3.51E19	66,400
10	-	-	-	-	4.52E16	59,900

**Table 2. PERCENT OF VARIANCE EXPLAINED BY  
MODELS 52, 61 AND 53**

	<u><math>\sigma(i)</math></u>	<u><math>F(i)^1</math></u>	<u>MODEL 52</u>	<u>MODEL 61</u>	<u>MODEL 53</u>
THFI	15.5	92.1	90.4	92.8	91.5
PA	53.5	91.7	96.3	<0	93.1
A	30.6	52.4	54.0	55.3	52.6
OIL	38.1	65.9	95.4	96.6	96.0
HGO 1+2	12.1	94.1	47.2	75.1	90.6
LGO	5.9	98.8	71.5	75.2	78.4
NAPHT	6.1	99.4	91.6	88.4	72.7
C1-C4	10.9	99.7	98.5	98.7	98.9
TOTAL	N/A	92.5	84.4	81.4	90.0

<sup>1</sup> target, based on standard deviations for individual components

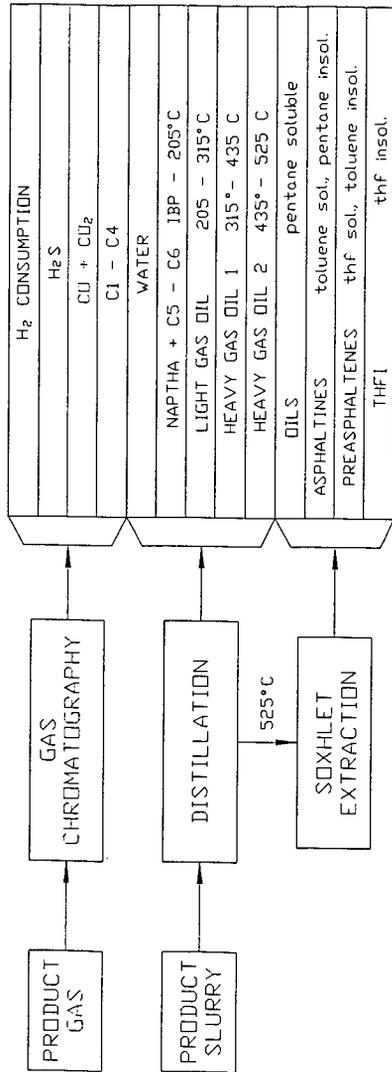


Figure 1. PRODUCT DEFINITION

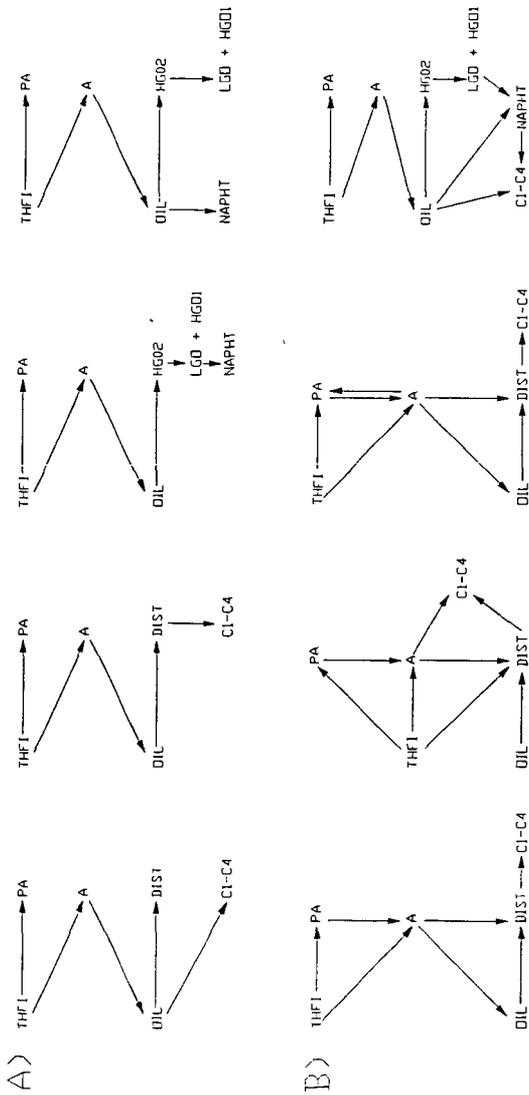


Figure 2. EXAMPLES OF SEQUENTIAL (A) AND PARALLEL (B) KINETIC STRUCTURES FOR COPROCESSING

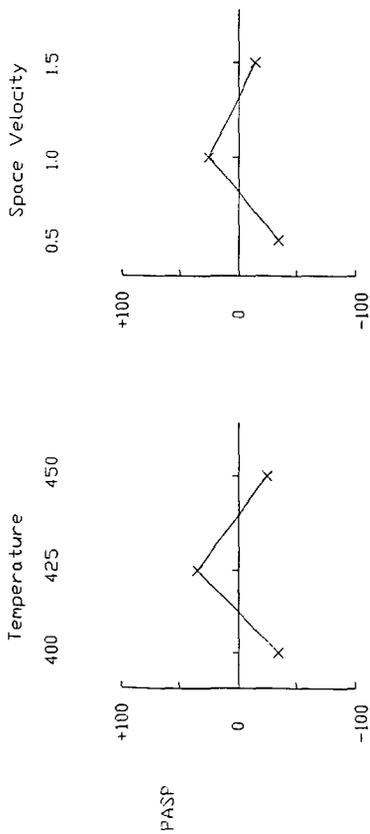


Figure 3. THE EFFECTS OF TEMPERATURE AND SPACE VELOCITY ON PREASPHALTENES COPROCESSING PRODUCTS

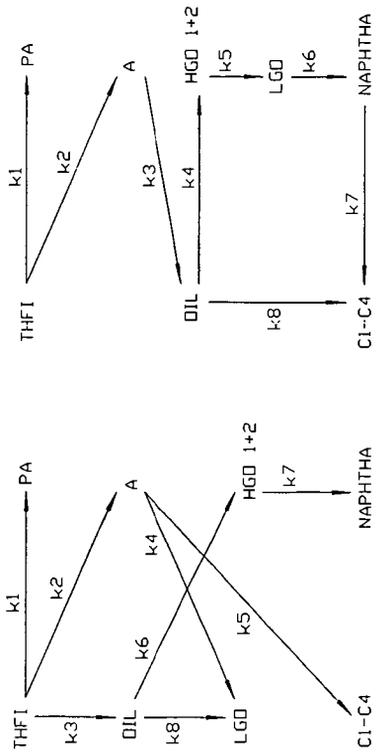
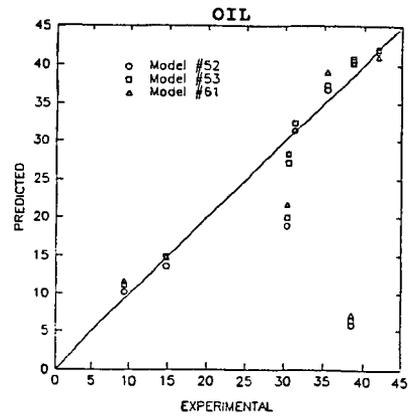
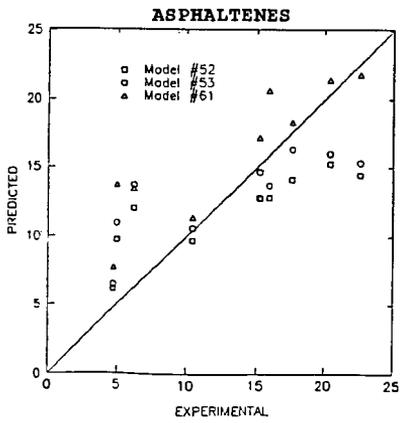
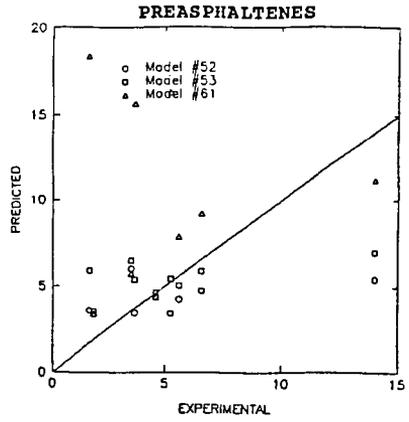
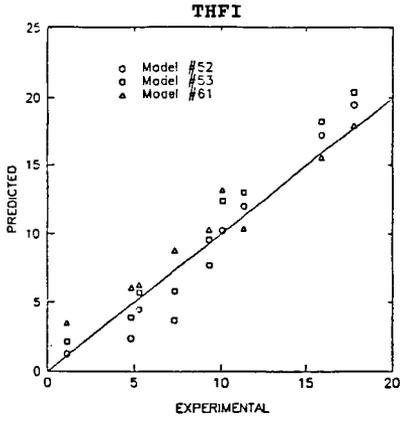


Figure 4. MODELS 52 AND 61



**Figure 5. PREDICTED vs EXPERIMENTAL DATA**

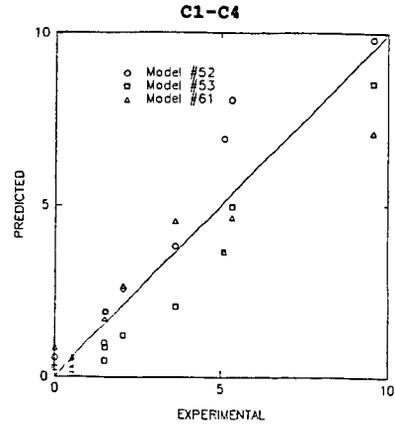
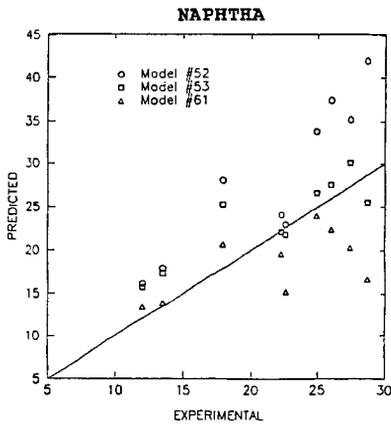
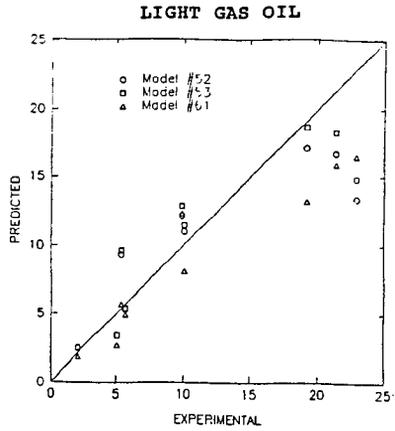
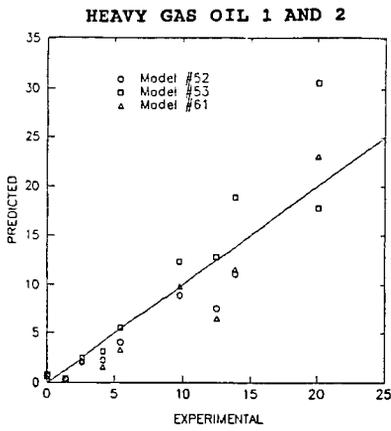


Figure 6. PREDICTED vs EXPERIMENTAL DATA

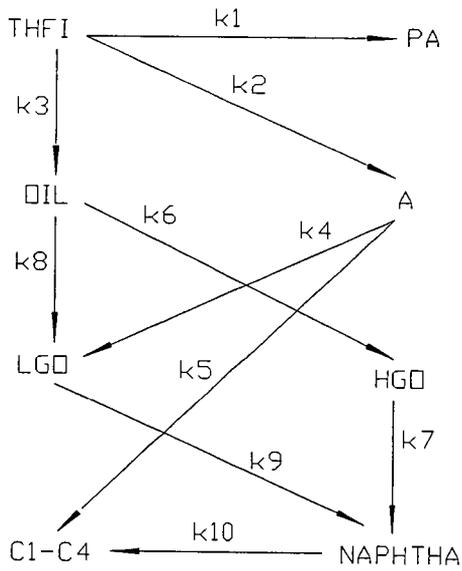


Figure 7. MODEL 53