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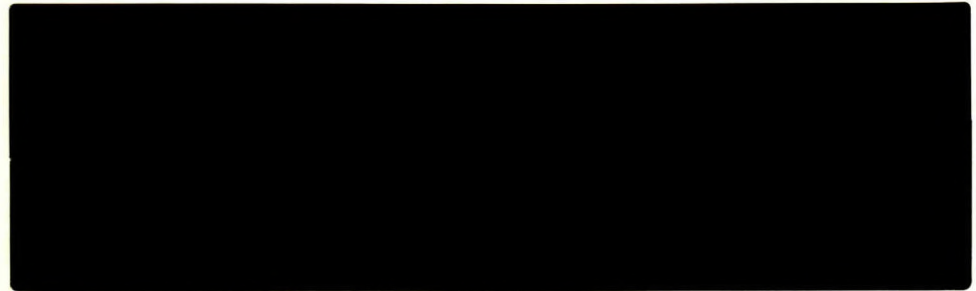
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*WRC 93-23 (J)*

1-4516

REACTIVITY OF CAUSTIC-TREATED OIL  
SAND COKE RESIDUES

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WESTERN RESEARCH CENTRE

June 1993

THIS WORK WAS SUPPORTED BY THE  
FEDERAL PANEL ON ENERGY RESEARCH  
AND DEVELOPMENT

Division Report WRC 93-23 (J)

# REACTIVITY OF CAUSTIC-TREATED OIL SAND COKE RESIDUES

by

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## ABSTRACT

Thermogravimetry (TG) and Fourier transform infrared (FTIR) spectroscopy have been used to study the pyrolysis behaviour and oxidative reactivity of molten caustic-treated and untreated oil sand cokes. The Syncrude fluid coke gave higher levels of CO/CO<sub>2</sub> during pyrolysis than Suncor delayed coke and CH<sub>4</sub> was only observed with the former. However, the CO/CO<sub>2</sub> evolution during pyrolysis of the caustic-treated coke residues was determined to be similar and higher than the values obtained with the untreated fluid coke. This is attributed to the displacement of sulphur in the coke matrix by oxygen during molten caustic leaching. The oxidation reactivity of the coke residues was found to increase with caustic treatment. This increase is attributed to the increased surface area of the cokes.

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## INTRODUCTION

Bitumen is recovered from the Athabasca oil sand deposits by the hot water process. Owing to the low hydrogen-to-carbon ratio in the crude bitumen, coking technology is employed in the upgrading process to produce synthetic crude oil. Suncor and Syncrude Canada Limited, (SCL) employ delayed and fluid coking technologies respectively [1]. In the coking process, the heavy ends which contain most of the sulphur and ash forming material are deposited. Currently about 3000 t of byproduct coke accumulate each day from these operations. The use of the coke residues for metallurgical purposes or as fuel for power generation is hindered by its high ash and sulphur contents [2,3]. Ityokumbul [4,5] has recently shown that molten caustic leaching of these coke residues was capable of producing coke products with ash and sulphur contents of less than 0.5%. Cokes with these low levels of impurities are amenable for use in the metallurgical industry and for power generation. For both the aluminum and thermal industry, the oxidation characteristics are important; the aluminum industry requires fuels with low oxidation reactivity while the converse is true for the thermal industry. The oxidation characteristics are generally obtained from the burning profile in an oxygen atmosphere.

The burning profile of the coke samples is obtained from the differential thermogravimetric (DTG) profile calculated from the weight-against-time curve of a thermogravimetric analysis. As described by Cumming [6], the burning profile may be characterized by four temperatures: (i) the initiation temperature where the loss of volatile matter commences,  $T_{vol}$ ; (ii) the temperature for the onset of combustion,  $T_{onset}$ ; (iii) the temperature at the peak weight loss,  $T_p$ ; and (iv) the burnoff temperature,  $T_{end}$ , where the combustion of the solid fuel is complete. However, for partially devolatilized solid fuels, only the last three are important. As explained by Wagoner and Duzy [7] in their pioneering work, the area under the peak weight loss curve is indicative of fuel burning characteristics in the furnace. Thus  $T_{end}$  may be used to determine the requirements for furnace residence time at high temperature to reduce carbon loss [7].

This study describes the application of thermogravimetry (TG), combined with FTIR spectroscopy of the evolved gases, to evaluate the oxidation characteristics of caustic-treated and untreated coke residues. The results obtained are compared with those obtained with green and calcined coke currently used in the aluminum industry. Since the aluminum industry requires cokes with low porosity, the BET surface area has also been determined for the treated and untreated coke residues.

## METHODS

### Materials

Untreated (feed) and molten caustic-treated samples of two cokes from the oil sand industry were studied. The fluid and delayed coke residues were obtained from SCL and Suncor operations, respectively, near Fort McMurray in Northern Alberta. The SCL coke was previously ground to minus 60-mesh and was sieved into minus 60 plus 100-mesh, minus 100 plus 140-mesh, and minus 140-mesh fractions. The Suncor coke was dried in an oven at 105°C for 6 h prior to grinding and then sieved into plus 40-mesh, minus 40 plus 60-mesh, minus 60 plus 100-mesh, and minus 100-mesh size fractions. For the studies reported here, only the minus 60 plus 100-mesh and minus 40 plus 60-mesh fractions of the SCL and Suncor cokes respectively were used.

The caustic-treated coke samples were prepared by mixing the feed coke samples with sodium hydroxide and heating the mixture in a furnace for a specified time at a given temperature. Details of the procedure have been given previously [3-5]. Table 1 gives the treatment conditions for the samples used in this study. The results obtained were compared to green and calcined coke samples obtained from Alcan Research and Development Centre in Québec.

### Instrumentation

The TG-FTIR instrument used was from BOMEM Inc. (Québec, Québec) and consists of a Dupont TG 951 whose purge gas outlet opens into a 16-pass gas cell connected to a BOMEM MB-100 FTIR spectrophotometer equipped with a narrow-band MCT detector. The helium purge gas flowed through the TG sample compartment at 0.0142 m<sup>3</sup>/h. Data collection and post-run analysis were handled using BOMEM and Lab Calc (Galactic Industries Inc., Salem, New Hampshire) software.

### Procedure

Approximately 10 mg of sample were heated in the TG at a rate of 20°C/min from 30 to 950°C, held for 5 min, cooled to 350°C and then heated again to 950°C at 20°C/min, this time in a 10% oxygen atmosphere. The thermocouple and balance readings were monitored and the data recorded as the temperature and weight percent of the sample against time.

An IR spectrum of the evolved gases was taken every 30 s during the TG run. For these experiments the software was set up to analyze the spectra for the evolution of the gases H<sub>2</sub>O, CO<sub>2</sub>, CO, CH<sub>4</sub>, SO<sub>2</sub>, and NH<sub>3</sub>. Gas calibration spectra used in this analysis were obtained from Advanced Fuel Research (East Hartford, Connecticut). The software

calculates a gas evolution curve that depicts the evolution rate in weight percent per minute (based on the original sample weight), against time. The integral of this curve then provides quantitative data for the amount of gas evolved.

#### Calculation of Activation Energy

The oxidation of solid fuels is a heterogeneous reaction. The processes involved have been reviewed by Laurendeau [8] and include the transport of oxygen from the bulk gas phase to the reaction surface, surface reaction, and transport of gaseous products from the reaction surface to the bulk gas phase. Thus, the rate of such a reaction is dependent on the oxygen partial pressure and the concentration of the solid fuel [9-13]. Accordingly, the rate of solid fuel combustion may be represented as:

$$-\frac{dw}{dt} = kf(w) \quad (1)$$

where  $k$  is the intrinsic rate constant and  $f(w)$  is some function, based on the reaction mechanism, of the amount of sample,  $w$ , remaining. For the case of solid oxidation, the function  $f(w)$  takes the form:

$$f(w) = P_{O_2}^m w^n \quad (2)$$

where  $m$  and  $n$  are the orders of the reaction based on oxygen and solid fuel respectively. For the solid fuel, the general consensus is that  $n$  is unity [14]. As reviewed by Smith [15], the value of  $m$  varies from 0 to 1.0 in agreement with the rate expression given by Lewis and Simons [10] for the oxidation of solid fuels. Recently, Tugluhan et al. [13] have reported that the exponent  $m$  varies from 1.0 and 1.32 for oxidation of oil shales below and above 300°C respectively. However, this difference in the value of  $m$  is attributed to volatilization of low-molecular-weight compounds which are oxidized in the gas phase. For oxidation in the presence of a large excess of oxygen, the oxygen partial pressure may be considered to be constant, and it may be lumped into the rate constant  $k$  to obtain:

$$-\frac{dw}{dt} = k'w \quad (3)$$

where



$$k' = kP_{O_2}^m \quad (4)$$

Using this equation and data from the thermogram one can calculate  $k'$  at different temperatures for low burnoffs (typically less than 15%). The activation energy can then be calculated using the Arrhenius equation:

$$k' = k_o e^{-E_a/RT} \quad (5)$$

where  $E_a$  is the activation energy,  $k_o$  is the frequency factor, and  $R$  is the gas constant.

This is a rather empirical approach but is sufficient for the purpose of this study which is to compare the activation energies of samples run in a TG instrument in exactly the same manner.

## RESULTS AND DISCUSSION

### Composition of Coke Samples

The compositions of the coke samples used in this study are given in Table 2 which also shows how these values compare to allowable levels for anode coke in the aluminum industry. A comparison of the feed materials with Alcan green coke clearly show that the untreated oil sand cokes were not suitable for use in the aluminum industry. However, the results suggest that the Suncor and Alcan green coke may have been produced by the same coking process since they both have low surface areas in comparison to the SCL fluid coke. The difference in the surface areas of the untreated oil sand coke residues is explained by differences in the coking processes. For example, we note that the partial combustion of fluid coke samples to provide heat for the coking reaction removes volatile hydrocarbons from the coke, leaving behind a porous structure.

As discussed previously [3,4], the results in Table 2 show that molten caustic leaching of these cokes was effective in reducing ash and sulphur contents; however, the surface areas of the caustic-treated samples were increased considerably. Since the coke structure is thus weakened by caustic treatment, the product may not be suitable for use in the aluminum industry. The caustic treatment also reduced the vanadium content of cokes (Table 2). The recovery of this vanadium may improve the economics of the caustic treatment process.

The thermograms for the coke samples have two main weight loss regions, one for

the pyrolysis of the sample, and the second when the balance of the sample is oxidized. The temperature program used was selected to effect the removal of volatile hydrocarbons from these cokes which might otherwise lead to false ignition of the coke, as discussed later in this report. Figure 1 shows an example from a TG run of Suncor feed coke; the other coke samples had qualitatively the same profile.

#### Analysis of the Pyrolysis Period

For the Suncor feed coke sample the main gases evolved during pyrolysis were  $\text{H}_2\text{O}$  and  $\text{CH}_4$  with some  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{SO}_2$ , and  $\text{NH}_3$  (see Table 3 and Fig. 2). The Syncrude feed coke evolved similar gases except there was only a trace of  $\text{CH}_4$  and no detectable  $\text{NH}_3$  (see Table 3 and Fig. 3). The differences in the relative amounts of  $\text{CH}_4$  released from the untreated oil sand coke samples is attributed to the different coking technologies employed by SCL and Suncor. As indicated earlier, the partial oxidation of the SCL fluid coke to provide the heat for the coking reaction strips the coke residue of volatile hydrocarbons. In addition, the fluid coking process is carried out at a higher temperature. It is noteworthy that the Alcan green coke also gave off relatively large amounts of  $\text{CH}_4$  during the pyrolysis period. Table 4 gives the weight loss values for the various samples. The total weight percent of the evolved gases agrees with the actual weight loss observed, within experimental uncertainty.

The release of greater amounts of  $\text{CO}_2$  and  $\text{CO}$  in the alkali-treated samples over that of the feed samples, from both Suncor and Syncrude, showed that there was an increase of reactive carbonyl groups in the treated coke samples. This increase is attributed to the displacement of sulphur by oxygen during molten caustic leaching [3]. This explanation is consistent with the observed lowering in activation energy for hydrodesulphurization of oil sand coke following pretreatment with oxygen [16].

The higher levels of  $\text{CO}_2$  and  $\text{CO}$  in the feed SCL coke than in the feed Suncor coke are also explained by the increased reactive carbonyl groups produced during the partial combustion of the SCL coke.

The other major difference between feed and caustic-treated coke samples was that the treated Suncor samples had a much reduced  $\text{CH}_4$  content. The evolved amounts of the other gases,  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{CH}_4$  in the Syncrude coke were relatively unchanged from the feed to the treated coke.

Figure 4 shows a detail from the pyrolysis region for the Suncor feed coke (minus the  $\text{CH}_4$  peak) showing the profile for the release of  $\text{CO}_2$  and  $\text{SO}_2$  in this region. The persistence of water in the Suncor coke to temperatures as high as  $800^\circ\text{C}$  is consistent with previous observations [17].

### Analysis of the Oxidation Period

The onset ( $T_{\text{onset}}$ ), peak ( $T_p$ ), and end ( $T_{\text{end}}$ ) temperatures for the oxidation peaks of the samples used in this study are given in Table 4. The values reported in Table 4 are the averages of two to four measurements. Of these temperatures,  $T_p$  has been used to characterize the reactivity of the solid fuel [6,18]. In general, a highly reactive solid fuel will give lower values for the onset, peak, and end temperatures. For both oil sand cokes, caustic treatment resulted in a lower peak temperature but a greater peak weight loss rate (Table 4). However, the drop in peak temperature was more pronounced with the Suncor treated samples. This observation suggests that the oxidation reactivity of the oil sand cokes increased with caustic treatment, the increase being more pronounced with the Suncor coke. As expected, calcination of the Alcan green coke resulted in a slight lowering of the oxidation reactivity. This is attributed to the removal of volatile matter from the coke during the calcination process.

The major gas released during oxidation of the coke samples was  $\text{CO}_2$ . However, because of the large amounts released the absorption values from the IR spectra were outside the calibration region and so quantitative values for the gas could not be obtained. Of the other gases released, the major change in the evolved gases between the feed and treated coke samples was the significant reduction in the  $\text{SO}_2$  evolution (Table 5), as one would predict from the reduced sulphur content of the treated samples. While the absolute amounts of  $\text{SO}_2$  released are slightly lower than those determined from elemental analysis (see Table 2), the relative amounts are in good agreement. As seen in Figs. 5 and 6 the amount of  $\text{SO}_2$  evolved during pyrolysis of the treated coke samples was greater than that giving off during oxidation.

### Kinetic Analysis of the Oxidation Reaction

Perhaps a more relevant indicator of reactivity is the activation energy. The use of activation energy to describe the reactivity of a solid fuel permits the inference of a rate-controlling process. For example, mass transfer limitations, usually expected at high temperatures, would result in a lowering of the activation energy. For this calculation, values of weight and temperature within the region of the loss of the first 10wt% were used in Eq. 3 to calculate rate constants. The values for the activation energy calculated in this study are based on various assumptions as outlined in Methods. However, they can be compared to one another for the purposes of determining the effect of the caustic treatment on the reactivity of the coke, and possibly the rate-controlling process in the oxidation reaction. The results are given in Table 4.

The differences in the nature of the two oil sand feed cokes and the similarity of the

Suncor and Alcan green cokes is reflected in their activation energies. Data in Table 4 show that calcination of the Alcan green coke affected only coke reactivity. This is attributed to the sample treatment procedure; since the pyrolysis step employed in this study has been shown to remove the volatile matter from the green coke, the green and calcined cokes may be expected to behave similarly during the oxidation cycle. The activation energy determined for SCL feed coke was similar to that reported for char oxidation [9]. For the SCL cokes, caustic treatment resulted in an increase in the activation energy while the converse was true for Suncor samples. The reasons for this observation are not entirely clear but may be related to mass transfer limitations and/or non-isothermal behaviour.

In order to explain the differences in the activation energy for the caustic-treated samples, the rate constant at the DTG peak was calculated. Using this value of the rate constant and the Arrhenius relationship determined for the different cokes, the average particle temperature was calculated ( $T_{p, cal}$ ). These results are summarized in Table 6.

The SCL feed, Alcan green, and Alcan calcined samples gave calculated values of particle temperature which agreed closely with the observed values, the maximum difference being +21°C. Since this difference is indicative of the temperature difference between the gas phase and the solid surface [9], these results indicate that for all practical purposes, the SCL feed and Alcan cokes may be considered to be operating under isothermal conditions. By contrast, the Suncor feed sample is shown to exhibit a temperature difference of -64°C, thus indicating that the gas phase was hotter than the average particle temperature. On the other hand, the caustic-treated coke samples all show that the particle was hotter than the gas, the difference being higher with the Suncor cokes. This is explained on the basis of increased surface reaction with the opening and even widening of the pore openings with caustic treatment. Since heat removal by the gas may not be efficient, the temperature of the particles increases. The observations in the present study are reasonable as Sergeant and Smith [9] have shown that film temperature differences ranging from 20-86°C may exist for 2% burnoff of 70  $\mu\text{m}$  particles. As reviewed by Laurendeau [8], the activation energies computed when large temperature differences between the particle and the gas are present may be a factor of two higher than the correct value. It is apparent from the foregoing that non-isothermal behaviour may be a factor in our kinetics studies. The activation energies determined in this study are in the range corresponding to an oxygen exponent of 0.5 [8].

## CONCLUSIONS

The major effects of alkali treatment of the feed cokes were to increase surface area and decrease ash, sulphur, vanadium, iron, silica, aluminum and sodium content. Owing to the increased porosity of the caustic-treated oil sand coke samples, they are not suitable for use in the aluminum industry. However, there is an enhanced oxidative reactivity of the caustic-treated samples with complete burning being observed at temperatures of 640°C and 600°C for SCL and Suncor coke samples respectively. They are therefore suitable for use in power generation: the product could be blended with a coal of a suitable volatility for use as a thermal fuel.

While molten caustic leaching of the oil sands may be an expensive process, the regeneration of the residual caustic, and recovery of the sulphur and vanadium from the leachate may considerably improve the process economics while at the same time solving the current coke accumulation problem. Steam gasification of the caustic-treated cokes may be studied as a potential source for hydrogen that is required in the upgrading process.

## ACKNOWLEDGEMENTS

The delayed oil sand samples were supplied by Suncor, the fluid coke samples by Dr. O.I. Ogunsola, and the Alcan green and calcined coke samples by Ms. Lise Castonguay. The award of a Visiting Fellowship to MTI by Energy, Mines, and Resources Canada is greatly appreciated.

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Table 1. Conditions for the alkali treatment of the coke samples used in this study.

Sample	Alkali Treatment Conditions	
	Temperature (°C)	Time (min)
Syncrude coke samples:		
68	400	45
69	400	30
70	400	15
98	450	12
Suncor coke samples:		
71	400	60
73	400	30
99	450	9
100	450	15

Table 2. Composition of coke samples

Sample	Ash (wt%)	Surface Area (m <sup>2</sup> /g)	Sulphur Removal (%)	S (ppm)	V (ppm)	Fe (ppm)	Si (ppm)	Al (ppm)	Na (ppm)
Syncrude Feed	7.96	16.7	0.0	71000	1460	6350	20400	9820	1920
68	0.37	377	97.4	1850	300	445	1430	415	135
69	0.28	425	98.8	850	235	66	2090	340	120
70	0.47	92	89.7	7310	610	44	2290	375	140
98	0.32	288	98.5	1060	210	34	1190	450	82
Suncor Feed	3.63	0.18	0.0	65000	1060	2080	9650	4960	325
71	1.17	251	94.5	3570	320	145	2060	1090	2170
73	0.78	418	98.1	1230	385	96	1150	425	1020
99	0.72	180	97.8	1430	580	235	1940	475	1220
100	0.73	270	99.6	260	355	520	1650	465	620
Alcan Green	0.30	0.80	----	31000	----	----	----	----	----
Alcan Calcined	0.18	4.50	----	31000	360	55	940	165	76
Allowable levels <sup>a</sup>	----	----	----	----	60	600	400	---	1200

<sup>a</sup> Allowable levels for coke use in the aluminum industry [20].



Table 3. Mass of gases evolved during the pyrolysis of coke samples as determined by FTIR spectrometry

Sample	Mass of Gases Evolved During Pyrolysis (wt%) <sup>a</sup>					
	CO <sub>2</sub>	CO	SO <sub>2</sub>	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> O
Syncrude Feed	3.3 ± 0.1	2.2 ± 0.1	0.3 ± 0.1	0.06 ± 0.01	0	11 ± 3
68	5.6 ± 0.6	10.1 ± 1.1	0.2 ± 0.2	0.05 ± 0.07	0	10 ± 1
69	5.1 ± 0.3	9.0 ± 0.7	0.14 ± 0.07	0.06 ± 0.06	0	4 ± 2
70	4.4 ± 0.6	7.2 ± 0.1	0.2 ± 0.2	0	0	7 ± 7
98	8 ± 2	11 ± 3	0.24 ± 0.01	0.11 ± 0.02	0	10 ± 4
Suncor Feed	1.1 ± 0.2	1.3 ± 0.1	0.23 ± 0.08	4.0 ± 0.2	0.18 ± 0.01	8 ± 4
71	6.8 ± 0.1	10.7 ± 0.9	0.13 ± 0.06	0.09 ± 0.01	0.14 ± 0.01	0.3 ± 0.4
73	5.8 ± 0.7	10.4 ± 0.9	0.11 ± 0.04	0.09 ± 0.02	0.08 ± 0.02	9 ± 6
99	6.9 ± 1.1	9.8 ± 1.9	0.19 ± 0.07	0.24 ± 0.03	0.16 ± 0.02	14 ± 2
100	7.2 ± 0.3	10.4 ± 0.8	0.10 ± 0.01	0.14 ± 0.06	0.11 ± 0.01	10 ± 4
Alcan Green	1.6 ± 0.3	1.7 ± 0.1	0.3 ± 0.2	3.18 ± 0.06	0.21 ± 0.03	3 ± 2
Alcan Calcined	2.1 ± 0.5	0.09 ± 0.05	0.2 ± 0.2	0	0	5 ± 7

<sup>a</sup> Weight percent of initial sample weight.

Table 4. Pyrolysis weight loss and kinetic data for oxidation of coke samples

Sample	Pyrolysis Weight loss (wt%)	Ash <sup>a</sup> (wt%)	Oxidation T <sub>onset</sub> (°C)	Oxidation T <sub>end</sub> (°C)	Weight Loss Peak-Rate (wt%/min)	E <sub>a</sub> (kJ/mol)
Syncrude Feed	8.3 ± 0.3	8.0	515 ± 1	817 ± 4	11.0 ± 0.2	111
68	15.0 ± 0.3	0.4	510 ± 2	636 ± 11	49.0 ± 6.4	195
69	15.1 ± 0.8	0.3	520 ± 3	640 ± 2	51.3 ± 2.0	196
70	14.5 ± 0.4	0.5	501 ± 5	641 ± 8	42.0 ± 0.7	253
98	16.5 ± 0.6	0.3	502 ± 6	645 ± 4	27.6 ± 0.7	200
Suncor Feed	11.4 ± 0.3	3.6	549 ± 4	824 ± 5	11.6 ± 0.5	209
71	18.7 ± 1.6	1.2	488 ± 1	597 ± 6	60.6 ± 0.3	177
73	16.7 ± 0.9	0.8	483 ± 8	600 ± 2	54.5 ± 0.2	153
99	17.9 ± 0.2	0.7	419 ± 13	575 ± 11	60.0 ± 2.4	116
100	17.6 ± 0.7	0.7	446 ± 4	588 ± 2	59.4 ± 2.1	139
Alcan Green	13.7 ± 0.9	0.3	534 ± 2	739 ± 2	20.4 ± 0.8	230
Alcan Calcined	1.9 ± 0.4	0.3	575 ± 13	770 ± 9	29.4 ± 3.0	232

<sup>a</sup> Ash at end of oxidation stage.

Table 5. Mass of gases evolved during the oxidation of coke samples as determined by FTIR-spectrometry.

Sample	Mass of Gases Evolved During Oxidation (wt%) <sup>a</sup>					
	CO <sub>2</sub>	CO	SO <sub>2</sub>	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> O
Syncrude Feed	O.S. <sup>b</sup>	5.0 ± 0.4	5.1 ± 0.2	0.03 ± 0.01	0.06 ± .02	0
68	O.S.	4.8 ± 1.2	0.06 ± 0.09	0	0.11 ± .01	0.3 ± 0.2
69	O.S.	3.4	0.1 ± 0.1	0	0.12 ± .02	0.4 ± 0.3
70	O.S.	4.2	0.5 ± 0.1	0	0.10 ± .01	0.2
98	O.S.	3.6 ± 0.3	0.06 ± .09	0.02 ± 0.04	0.10 ± .02	0.3 ± 0.2
Suncor Feed	O.S.	5.2 ± 0.8	4.5 ± 0.2	0.01 ± 0.01	0.06 ± .08	0
71	O.S.	3.3 ± 1.6	0.02 ± 0.04	0	0.1	0.4 ± 0.2
73	O.S.	3.4 ± 1.0	0.01 ± 0.01	0	0.10 ± .01	0.2 ± 0.2
99	O.S.	3.2 ± 0.6	0	0	0.12 ± .01	0.4 ± 0.1
100	O.S.	2.6 ± 0.7	0	0	0.11 ± .01	0.3 ± 0.1
Alcan Green	O.S.	3.9 ± 0.2	1.9 ± 0.1	0	0.10 ± .01	0.8 ± 0.8
Alcan Calcined	O.S.	4.3 ± 0.3	2.1 ± 0.2	0	0.08 ± .02	0.2 ± 0.4

<sup>a</sup> Weight percent of initial sample weight.

<sup>b</sup> Off scale: Amount of CO<sub>2</sub> exceeded the limits of the calibration region.

Table 6. Determination of film temperature gradient at oxidation weight-loss peak

Sample	Arrhenius Constants <sup>a</sup>		$k_{\text{peak}}^{\text{b}}$ (min <sup>-1</sup> )	$T_{\text{p, cal}}$ (°C)	$T_{\text{p, cal}} - T_{\text{p}}$ (°C)
	$k_o$ (min <sup>-1</sup> )	$-\frac{E_a}{R} \times 10^{-3}$ (K)			
Syncrude Feed	1.9 x 10 <sup>5</sup>	13.3	0.35	735	8
68	9.5 x 10 <sup>10</sup>	23.5	2.20	686	70
69	1.1 x 10 <sup>11</sup>	23.6	2.42	689	74
70	1.2 x 10 <sup>15</sup>	30.4	0.99	603	29
98	3.4 x 10 <sup>11</sup>	24.0	1.68	650	68
Suncor Feed	1.9 x 10 <sup>11</sup>	25.1	0.38	658	-64
71	1.9 x 10 <sup>11</sup>	21.3	3.27	673	106
73	5.2 x 10 <sup>8</sup>	18.3	2.93	693	118
99	5.6 x 10 <sup>6</sup>	14.0	1.84	664	137
100	1.4 x 10 <sup>8</sup>	16.7	2.01	651	106
Alcan Green	2.0 x 10 <sup>12</sup>	27.6	0.56	643	10
Alcan Calcined	9.1 x 10 <sup>12</sup>	27.9	0.64	687	21

<sup>a</sup> Values refer to Eq. 5.

<sup>b</sup> Calculated from the Eq. 5 and value of  $T_{\text{p}}$  (Table 4).

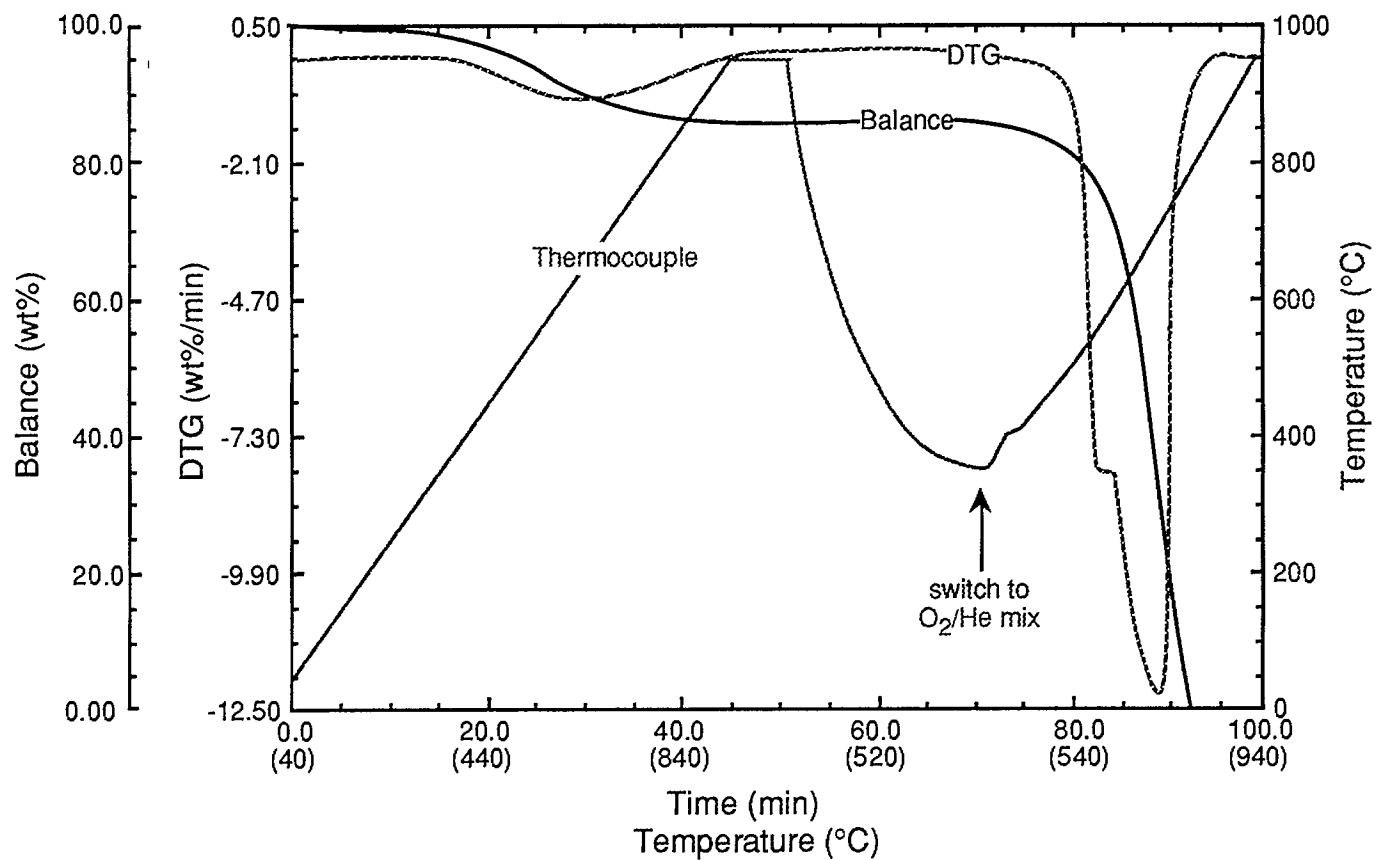


Figure 1. Thermogram from the TG-FTIR analysis of Suncor feed coke. The thick line shows the balance reading versus time, while the dashed line is the derivative (DTG).

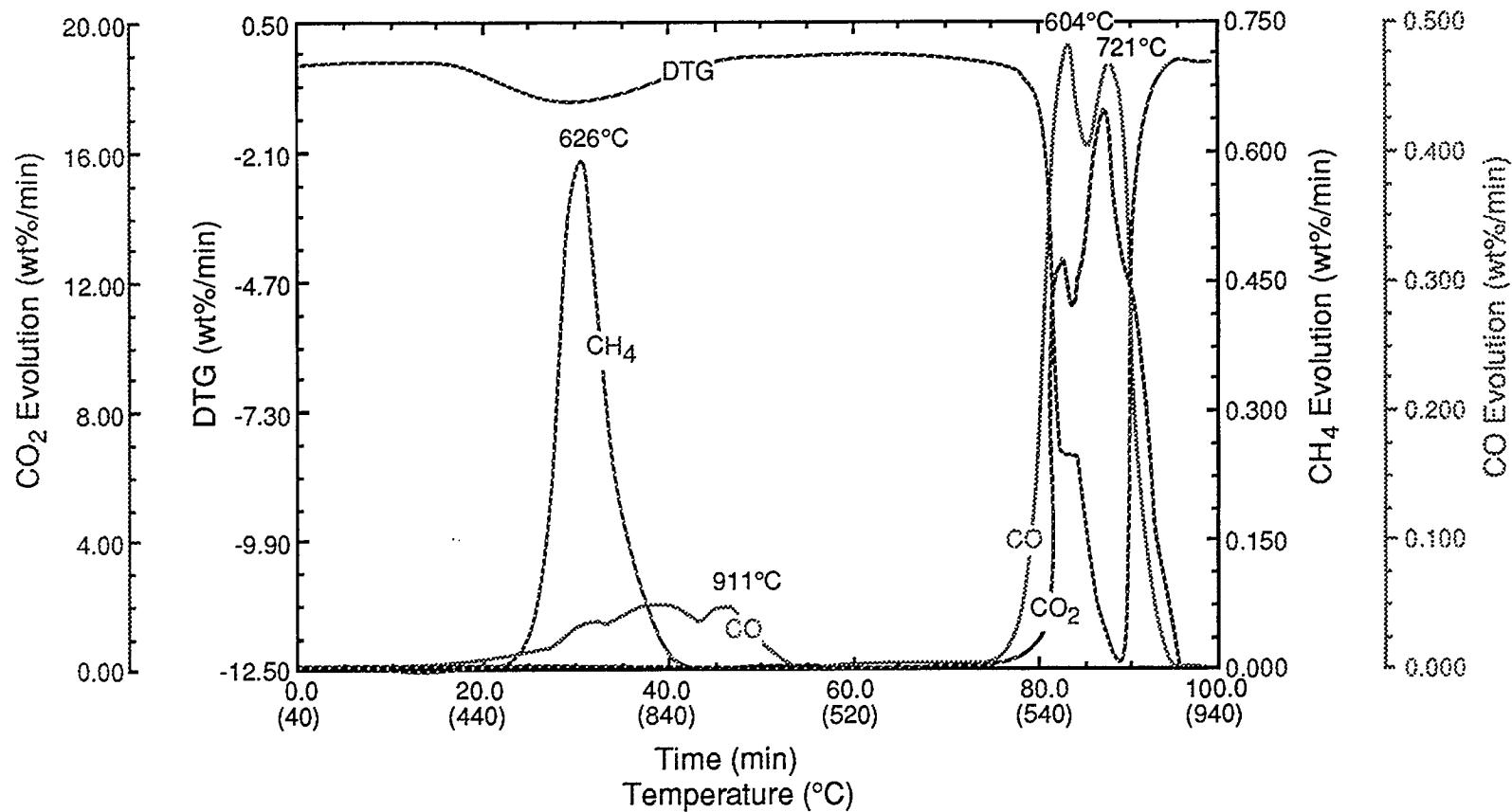


Figure 2. Graph showing the evolved gas curves from the TG-FTIR analysis of Suncor feed coke. See Fig. 1 for the thermal program used.

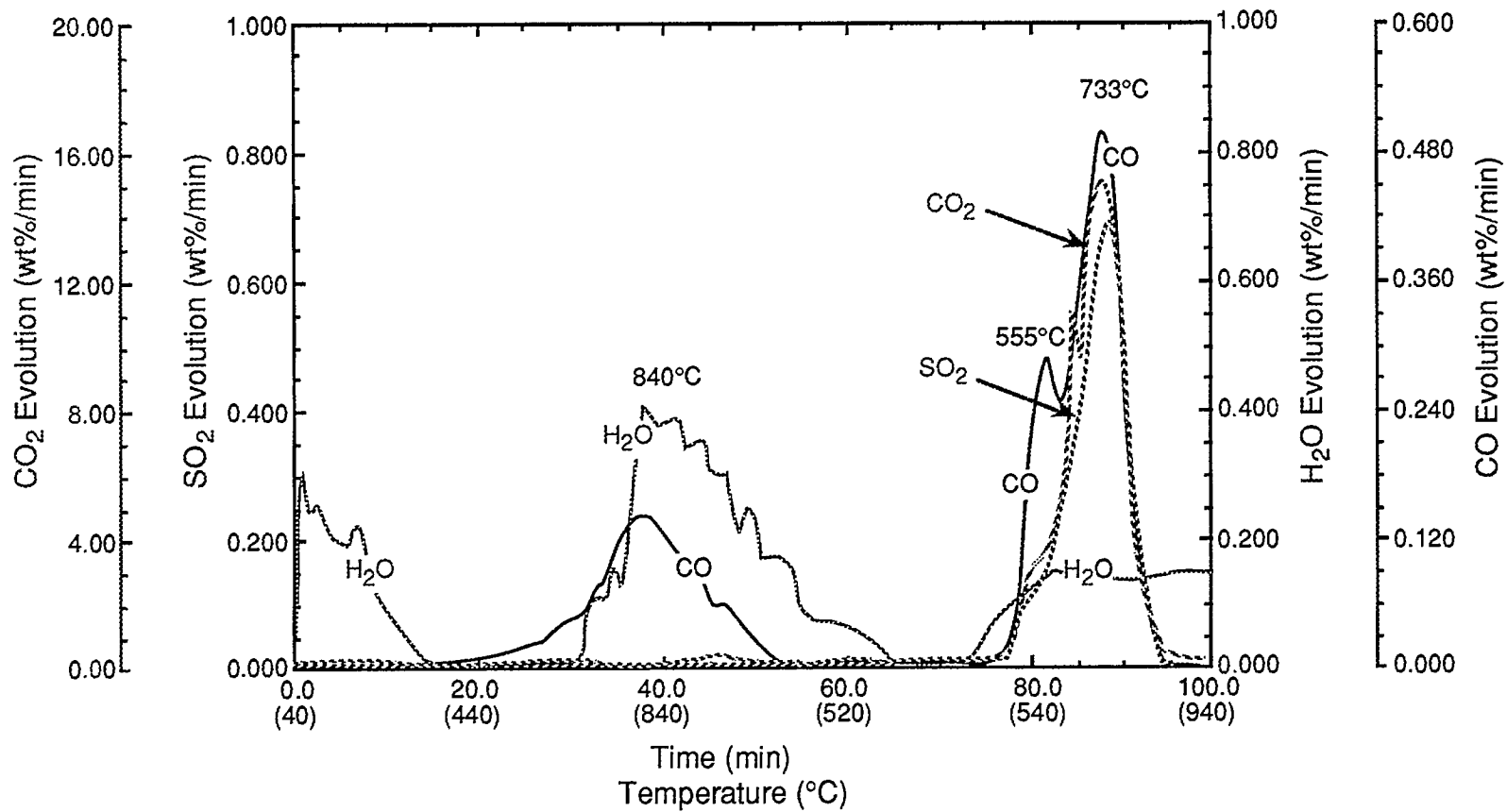


Figure 3. Graph showing the curves for selected gases evolved during the TG-FTIR analysis of Syncrude feed coke. See Fig. 1 for the thermal program used.

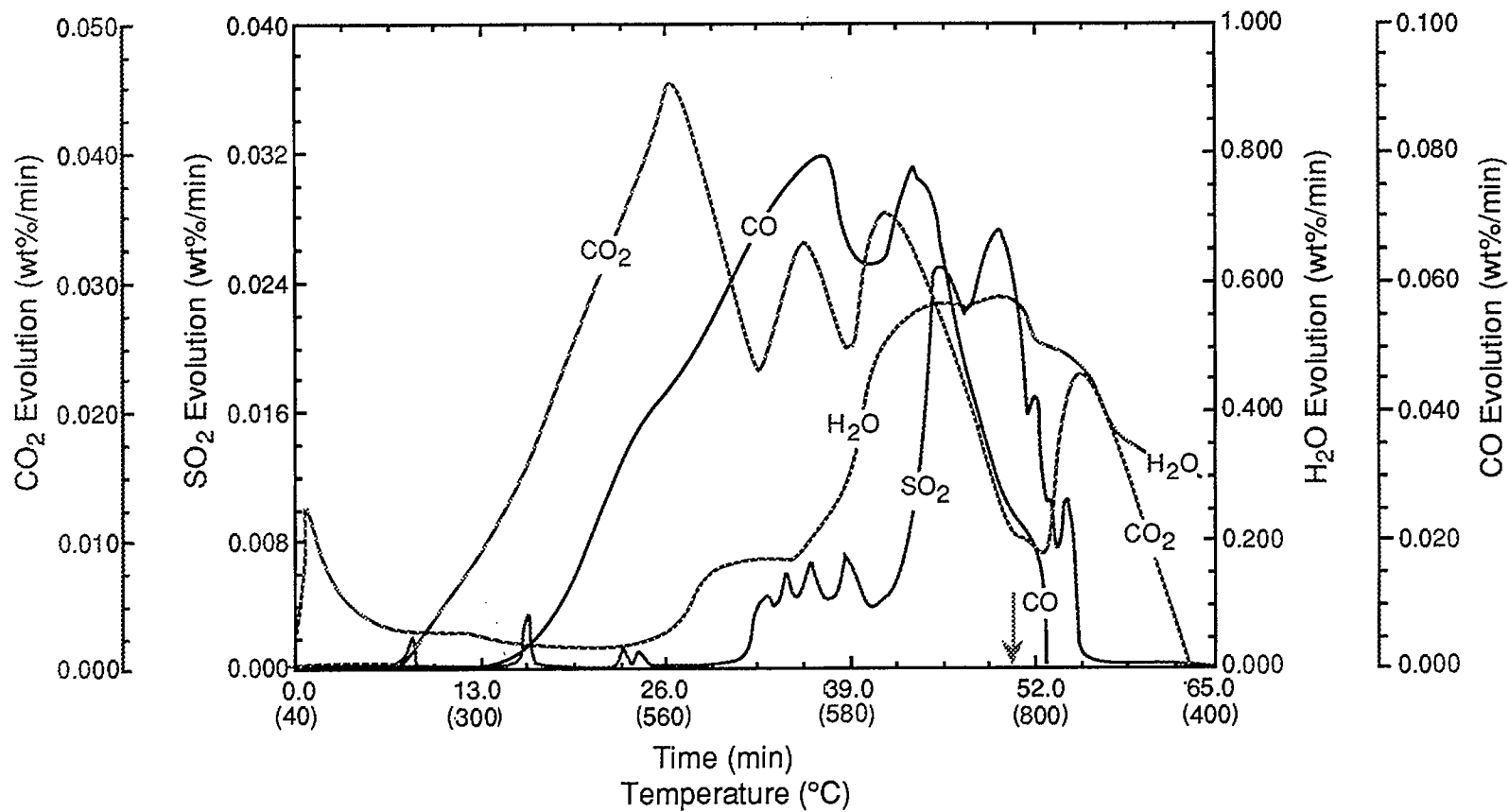


Figure 4. Graph showing detail of the pyrolysis region of selected gases from the TG-FTIR analysis of Suncor feed coke. The arrow marks the point at which the sample was cooled.



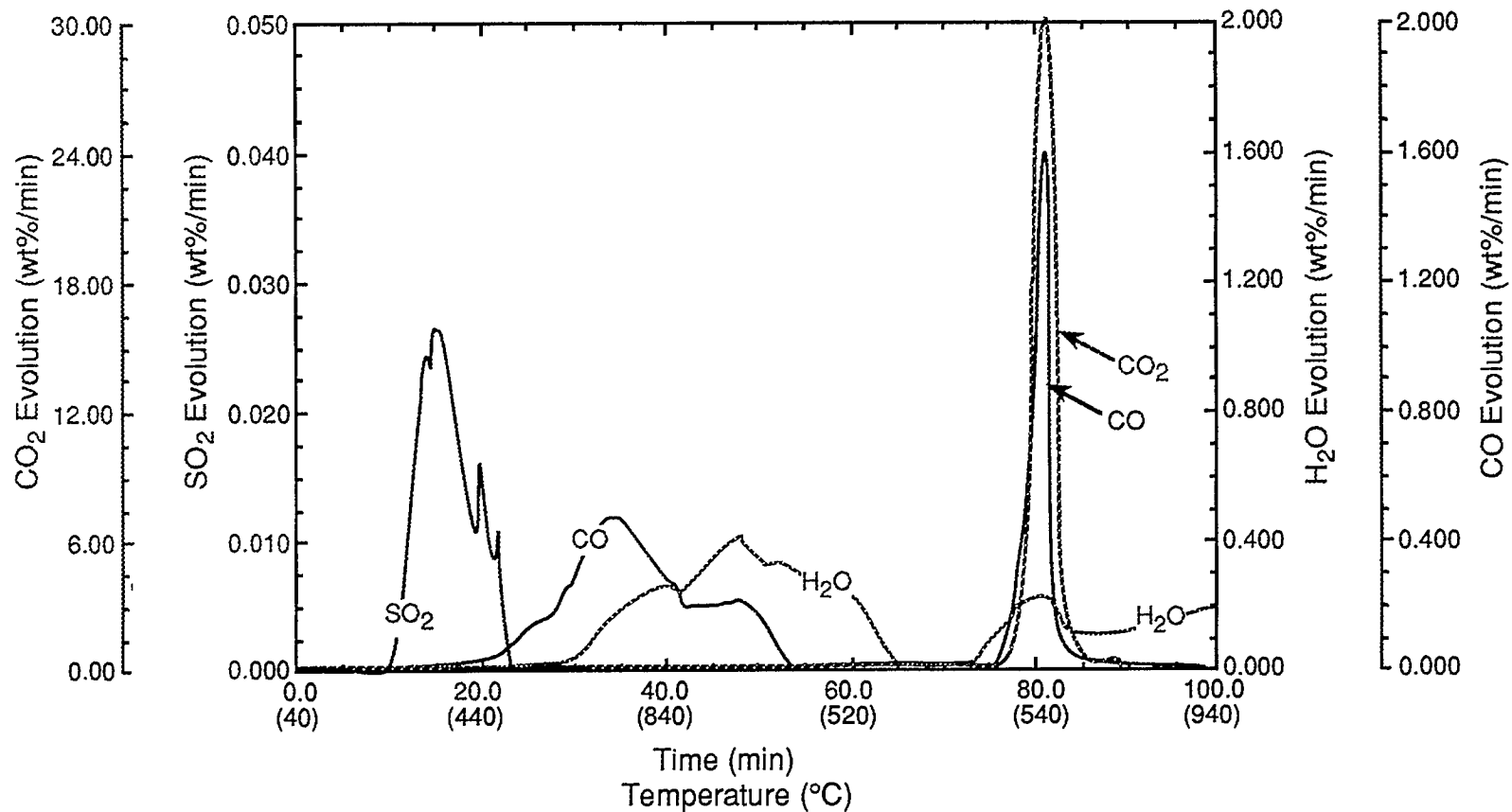


Figure 5. Graph showing the curves for selected gases evolved during the TG-FTIR analysis of alkali-treated Syncrude coke. See Fig. 1 for the thermal program used.

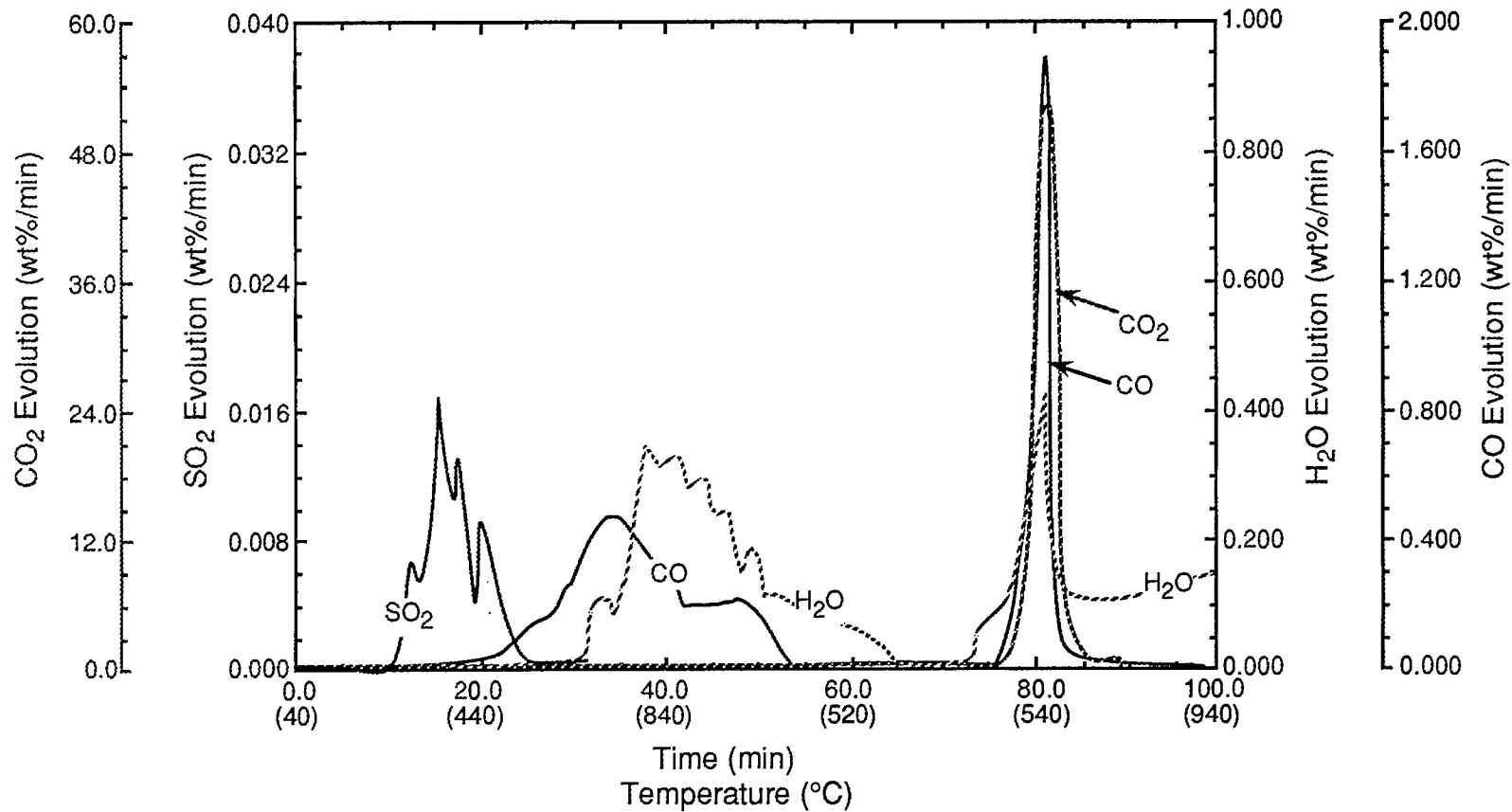


Figure 6. Graph showing the curves for selected gases evolved during the TG-FTIR analysis of alkali-treated Suncor coke. See Fig. 1 for the thermal program used.

