

APPLICATIONS OF THE THERMOGRAVIMETRIC ANALYSIS IN THE STUDY OF FOSSIL FUELS

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Key words: thermogravimetric analysis, fossil fuels, characterization

INTRODUCTION

Applications of thermal analysis in fossil fuel research date back as far as the techniques themselves. Thermogravimetry (TG) had been used by Somiya and Hirano in 1930 to determine the volatile yield of many coals (1). Advances in design of thermogravimetric analyzers (TGA) now allow experiments to be carried out simply and fast in high accuracy under various conditions from vacuum to high pressure (2-4). A TG method has been devised for the proximate analysis of coal with the results of the same precision and accuracy as BS and ASTM methods (5).

Thermogravimetric (TG) techniques have been used in our laboratory to characterize fossil fuel samples (6) and to study coal liquefaction kinetics, mechanisms, and processes (7-10). TGA has been providing sensitive, rapid, and reproducible measurements for those purposes. The various weight loss processes determined during the TG analysis reflect the physical and chemical structural changes during the conversion. Thermogravimetric analysis has other desirable features as well. First, only very small samples, usually about 30 mg, are required for each TG scan. Second, by suitable adjustments in the work-up procedures and the TG operating parameters, thermogravimetric analysis reveals important information concerning the reaction pathways. Besides, custom-built thermogravimetric techniques provide very flexible means and unique features for fossil fuel research (11-13).

Development and applications of the TG techniques in our laboratory are reported in this paper. These include 1). characterization of coal structure; 2). determining the liquefaction conversion and measuring the rate of the retrograde reactions occurring during coal liquefaction; 3). evaluating the thermal and catalyzed hydroprocessing of the coal-derived resids; and 4). determining the boiling range of liquid fuels. Various effects including the TG operating variables, such as heating rate, purge gas type (e.g. H_2 or N_2), gas flow rate, and modification of the TG sample pan as well as a method for the development of a custom built thermogravimetric system are also discussed in this paper.

EXPERIMENTAL

Apparatus. The Thermogravimetric Analyses (TGA) were performed with a Model 51 TGA (TA Instruments, New Castle, Delaware).

Procedures. An approximately 30-60 mg sample (e.g. coal, coal liquefaction residue, coal liquid, coal-derived resid, etc.) was loaded in a quartz pan and mounted in the instrument. Selected TG scans were processed using an 11-point smoothing filter of the Linear Regression & Error Analysis procedure (14). The program of manipulation of the TG operating variables was determined by the objectives of the particular experiment.

Materials Studied. Eight coals of rank from lignite to l.v. bituminous were obtained from the Argonne Premium Coal Sample bank. Analytical values of these coals are given in the User's Handbook (15). Two 850°F distillation residue oils (resids), one derived from Wyodak subbituminous coal and another from Pittsburgh bituminous coal, were obtained from the Wilsonville Pilot Plant Runs 259 and 260, and prepared and composited by CONSOL Research. At room temperature, these two resids are solid and only partially soluble in tetralin.

RESULTS AND DISCUSSION

Coal Structure and Composition. A representative TG scan on the Illinois #6 coal is shown in Figure 1. In brief, two stages, i.e., 1) the heating rate at 10 °C/min to 950°C in nitrogen and hold for 7 min; and 2) the oxidation at 950°C, provided measures of Volatile Matter (VM), Fixed Carbon (FC), and Ash. Ash content measured by TGA is in close agreement with that determined by ASTM D3174. When a coal sample is brought to 110 °C in nitrogen and hold for 10 min, the weight loss is a measure of the moisture content (16).

The differential of the weight loss (DTG) curve highlights the various TG processes more clearly. The DTG curve for Illinois #6 shows a pattern which is more complex than many of the other Argonne coals. This becomes even more distinct and complex if the heating rate is slowed down to about 1 °C/min (6).

Thermogravimetric analyses were also run in a hydrogen atmosphere. This provided additional information regarding the structure of coal. (For safety reasons, hydrogen MUST be thoroughly displaced by nitrogen before air or oxygen is introduced.) DTG curves of the eight Argonne Premium Coals in nitrogen and in hydrogen show similar patterns. However,

the Volatile Matter yields at heating rates from 10 °C/min to 200 °C/min are consistently higher, and therefore the Fixed Carbon yields are lower, in hydrogen than in nitrogen. More importantly, the heating rate has a strong effect on the yields of Volatile Matter in either hydrogen or nitrogen. In hydrogen, the Volatile Matter yields decrease somewhat as the heating rate increases. This may be because the pyrolysis time is shorter at higher heating rate, providing less time for reaction with the molecular hydrogen to form more volatile products. However, in nitrogen, the Volatile Matter yields increase with increasing heating rate. This phenomenon may be because, at the low heating rates, the unquenched free radicals react to form more retrograde products (fixed carbon). This is consistent with the flash pyrolysis process, where the oil and gas product yields increase with increasing heating rate.

TGA provides an objective measure of coal rank. DTG curves scanned in 100 cm³(STP)/min nitrogen at 10 °C/min for the eight Argonne Premium Coals (which were dried in a vacuum oven with a nitrogen purge at 105 °C for 48 hours before use) are shown in Figure 2. These coals range ranking from lignite to l.v. bituminous. This plot clearly shows the gradual shift of peak temperature as the coal rank increases from Lignite to low volatile bituminous coal. However, the peak height increases to a maximum at about 81 wt% (daf) Carbon and then decreases as the rank increases.

Coal Liquefaction Studies. A Short-Contact-Time Batch Reactor (SCTBR) was used to run coal liquefaction. This reactor apparatus allows the heat up and quenching of the process stream to and from reaction temperature in about 0.3 seconds, respectively. The design and operation of such a SCTBR reactor system have been described in detail elsewhere (17,18). After a liquefaction run, the product mixture was filtered and the solid residue washed with fresh tetralin thoroughly, then rinsed with methylene chloride to remove residual tetralin, and dried in a vacuum oven with a nitrogen purge at about 105 °C for 48 hours. This resulted in the production of a liquid filtrate, which consisted mainly of tetralin and dissolved coal liquids, and a solid filter cake, of unconverted and/or partially converted solid coal residue.

During coal liquefaction, the coal liquids are extracted into the tetralin solvent. However, the mineral matter of the coal remains with the solid coal residue and is insoluble in tetralin, as proven by the TG scan on the liquid filtrate (8,19). Since the ash is not consumed during the liquefaction and remains in the solid, conversion to the tetralin-soluble oils can be derived based on an ash-balance (8,17):

$$\text{Conversion} = \left(1 - \frac{A_o}{A_s}\right) \times 100\% \quad (1)$$

where A_o and A_s are the weight fractions of ash in the control sample and in the liquefaction residue, respectively. The control sample is the original coal which is processed exactly as a liquefaction residue except at ambient temperature. When the liquefaction is carried out in the presence of an inorganic catalyst, the conversion calculation must include an ash value corrected for the ash derived from the catalyst.

The thermal and catalyzed liquefaction conversions of Illinois #6 coal in tetralin at 390 °C are shown in Figure 3. In the thermal liquefaction, three distinct phases in the process were observed, i.e., a very rapid conversion followed by an induction period and then a slower liquefaction of the coal structure. The initial rapid conversion in the first minute is due to the physical extraction of a soluble fraction of the coal into the hot tetralin. This is followed by an induction period and then the slow conversion of the coal structure to liquid products. The induction period observed is actually a pseudo induction period. This induction period is a transition interval which is due to the simultaneous occurrence of two processes, a very rapid extraction and a relatively slower liquefaction of the coal structure. In fact, as the temperature increases, the induction period steadily becomes less pronounced as the rate of break down of the coal structure increases and becomes closer in reaction rate to the extraction step itself (10). That the induction period is not due to the build up of free radicals is also proven by ESR data (20,21). In the catalyzed liquefaction, the pseudo induction period is, as expected, diminished and the subsequent conversion is much faster for the catalyzed than the thermal liquefaction. More importantly, the retrograde process, leading to form tar, coke and char, is very significantly reduced in the presence of catalyst and hydrogen as is shown by the Fixed Carbon content in the residue as a function of liquefaction time (Figure 4). When the catalyzed liquefaction was run at higher temperature, the Fixed Carbon of the residue was even further reduced (Figure 5), suggesting that the precursors of the retrograde processes are being hydrogenated and stabilized during the catalyzed liquefaction. Liquid yields were thereby significantly improved (Figure 6).

DTG curves for partially converted coal liquefaction residues of Illinois #6 coal after liquefaction in tetralin at 390°C under 1000 psig nitrogen at selected contact times are

shown in Figure 7. The gradual disappearance of the two smaller peaks (one of them identified as FeS₂ conversion to FeS and S) clearly indicates that some chemical changes in the solid coal are taking place before the coal actually becomes liquid. In addition, the sensitivities of the production of VM in the residues to heating rate and to atmospheres of nitrogen and hydrogen are significantly changed as shown in Figures 8a and 8b for the unreacted original Illinois #6 coal and a liquefaction sample of Illinois #6 taken after 30 seconds at 390 °C, respectively. The profound changes shown in that short time suggests that even short exposure to donor solvent can significantly change the character of the coal before much actual liquefaction has taken place. This change may merely be the removal of a very unstable volatile fraction or actual stabilization by hydrogen transfer from the donor solvent.

Evaluating the thermal and catalyzed hydroprocessing of the coal-derived resids. The Short-Contact-Time Batch Reactor (SCTBR) was again used for the thermal and catalyzed hydroprocessing of the coal-derived resids. The resid reaction product workup procedure and determination of the thermal and catalyzed resid conversion have been described in detail elsewhere (8). The conversion of resid to tetralin soluble material was determined by relating the inorganic matter (ash) in the reacted resid with that of the unreacted resid. Un-catalyzed conversion of tetralin-insoluble resids to tetralin soluble products in this study was very low (< 10 wt%) under coal liquefaction conditions (410 - 440 C, 1500 psig H₂, 2 - 5 of tetralin to resid ratio). But, up to 80 wt% (ash-free basis) was solubilized in tetralin using sulfided Ni/Mo on alumina catalyst at 434°C for 10 min. Hydroprocessing at liquefaction conditions (see above), and particularly in the presence of Ni/Mo on alumina catalyst, was effective for converting tetralin-insoluble to tetralin-soluble material, and for reducing the average molecular weight (8). Up to 50 wt% of the resid was already tetralin soluble even at room temperature. Therefore, the tetralin solubility cannot be used as a measure of the resid converted to low boiling fuels. The actual conversion of resid represents the portion of the resid which is broken down in the hydroprocessing to low molecular weight material boiling below 850 °F. For that reason, additional technique(s) is required for measuring the degree to which the resids is converted to lower boiling products (i.e. below 850 °F).

An analytical TGA method for boiling range measurement, SimDis TGA, has been developed for that purpose. This SimDis TGA technique requires a change in the conventional TGA sample pan. It was devised with a small aperture at the top of the pan. The fundamentals, methodology, and experimental details of the SimDis TGA technique have been reported in the Symposium on New Analytical Methods for Characterizing Fossil Fuels and Derived Products in Chicago in 1995 (22). The boiling point distribution of Wilsonville # 258 resid liquid sample, which was determined by the SimDis TGA technique, is shown in Figure 9. This resid sample was hydroprocessed in tetralin using sulfided molybdenum naphthenate catalyst at 403°C for 60 minutes. The fraction of the resid liquid boiled below 850 °F (i.e. 850 °F) was 93.8 wt%, in which tetralin fraction was included. The following equation:

$$\text{Conversion (850 }^\circ\text{F)} = \text{TSF} \times \left(1 - \frac{\text{850 }^\circ\text{F}^+ \text{ in tetralin}}{\text{RSF in tetralin}}\right) \times 100\% \quad (2)$$

was used to evaluate the resid conversion to 850 °F during the thermal and catalyzed hydroprocessing. In Equation 2, TSF (Tetralin Soluble Fraction) was determined by ash content in the solid residue (8); RSF (Resid Soluble Fraction) and 850 °F⁺ fractions in tetralin were determined by running the ramp and SimDis TGA methods (8,22) on the resid liquid products, respectively. Preliminary studies show that, for the illustrative sample in Figure 9, TSF (Tetralin Soluble Fraction) determined by ash content of the solid residue was 67.8 wt%; 850 °F⁺ fractions in tetralin determined by the ramp method was 8.62 wt%. Conversion of the Wilsonville #258 resid hydroprocessed under those conditions to 850 F⁺ was 19.0 wt%.

Determining boiling point distribution of liquid fuels. In addition to the SimDis TGA method, which is capable of measuring the boiling point up to 1000 °C and briefly described in previous section, a custom-built thermogravimetric apparatus for distillation of liquid fuels was also developed in our laboratory (23). As an example, boiling point distribution of a crude oil analyzed using the custom-built thermogravimetric apparatus is illustrated in Figure 10.

CONCLUSION

Thermogravimetric analysis (TGA) of coal and resid liquids and coal and resid solid residues, which were produced in coal liquefaction and coal-derived resid hydroprocessing in the SCTBR (Short-Contact-Time Batch Reactor) apparatus, provides a sensitive, rapid, and reproducible means of studying the kinetics and mechanisms of fossil fuel conversion

processes. SimDis TGA and the custom built thermogravimetric system for distillation provide unique means to characterize liquid fuels for the boiling point distribution.

Thermogravimetric Analysis (TGA) provides information concerning the various weight loss processes that can be a reflection of the physical and chemical structure of fossil fuel samples. More importantly, this technique is also capable of yielding TG scanning parameters, such as Volatile Matter, Fixed Carbon, Ash, etc. to be used to monitor the fossil fuel conversion processes. A significant example is to determine the onset and rate of the retrograde reactions during the coal liquefaction process.

ACKNOWLEDGMENTS

The support of these studies by the Department of Energy under DE22-93PC93205 and by subcontracts from CONSOL Inc. under U. S. DOE Contract No. DE-AC22-89PC89883 and DOE Contract No. DE-AC22-94PC93054 is gratefully acknowledged.

The assistance and advice of F.P. Burke, R.A. Winschel and S.D. Brandes of CONSOL Inc in preparation and analysis of the resid and catalyst samples used in resid hydroprocessing are gratefully acknowledged. The use of Argonne Premium Coal Samples provided by Dr. Karl Vorres is also acknowledged.

Additional funds for purchase of thermal analysis equipment was provided by the University of Delaware.

REFERENCES

1. Somiya, T.; Hirano, S. *J. Chem. Soc. Ind. (Japan)* 1930, **33**, 737.
2. Schwartz, H.E.; Brownlee, R.G.; Boduszynski, M.; Su, F. *Anal. Chem.* **1987**, **59**, 1393.
3. Nie, X.; McClennen, W.H.; Liu, K.; and Meuzelaar, H.L.C. *ACS Fuel Chem Div Preprints* **38** (4), 1147 (1993).
4. Liu, K.; Jakab, E.; McClennen, W.H.; Meuzelaar, H.L.C. *ACS Fuel Chem Div Preprints* **38** (3), 823 (1993).
5. Ottaway, M. *Fuel* **1982**, **61**, 713.
6. Huang, He; Wang, Keyu; Klein, M.T.; W.H. Calkins *ACS Fuel Chem Div Preprints* **40** (3), 465 (1995).
7. Huang, He; Wang, Keyu; Calkins, W.H.; Klein, M.T. *ACS Fuel Chem Div Preprints* **39** (3), 741 - 746 (1994).
8. Huang, He; Calkins, W.H.; Klein, M.T. *I&EC Research* **33**, 2272-2279 (1994).
9. Huang, He; Wang, Keyu; Klein, M.T.; W.H. Calkins *Coal Science and Technology 24: Coal Science*, Eds J.A. Pajares and J.M.D. Tascon, Vol. II, p. 1207 (1995).
10. Huang, He; Wang, Keyu; Wang, Shaojie; Klein, M.T.; W.H. Calkins *ACS Fuel Chem Div Preprints* **40** (3), 550 (1995).
11. Massoth, F.E. *Chem. Tech.* 1972, May, 285.
12. Sears, J.T.; Maxfield, E.A.; Tamhankar, S.S. *Ind. Eng. Chem. Fundam.* 1982, **21**, 474.
13. Dean, J.W.; Dadyburjor, D.B. *Ind. Eng. Chem. Res.* 1988, **27**, 1754.
14. Wang, Keyu; Wang, Shaojie; Huang, He; Klein, M.T.; Calkins, W.H.; paper to be presented in the *Symp. on the Thermal Analytical Techniques*, March 24-29, 1996, in New Orleans.
15. Vorres, K.S. 'User's Handbook for the Argonne Premium Coal Sample Program' *ANL/PCSP-93/1*.
16. He Huang, D.M. Bodily, and V.J. Hucka *Proceedings 1993 International Conference on Coal Science*, 411-414.
17. Huang, He; Calkins, W.H.; Klein, M.T. *Energy and Fuels* **8**, 1304-1309 (1994).
18. Huang, He; Fake, D.; Calkins, W.H.; Klein, M.T. *Energy and Fuels* **8**, 1310-1315 (1994).
19. Calkins, W.H.; Huang, He; Klein, M.T. *Proceedings 1994 Pittsburgh Coal Conference* pps. 475-480.
20. Huang, He; Provine, W.D.; Jung, B.; Jacintha, M.A.; Rethwisch, D.G.; Calkins, W.H.; Klein, M.T.; Dybowski, C.R.; Scouten, C.G. *Proceedings of the International Conference on Coal Science, 1993*, Ed. K.H. Michaelian, Vol. I, 266.
21. Provine, W.D.; Jung, B.; Jacintha, M.A.; Rethwisch, D.G.; Huang, He; Calkins, W.H.; Klein, M.T.; Scouten, C.G.; Dybowski, C.R. *Catalysis Today*, **1994**, Ed. D.B. Dadyburjor and J.W. Zondlo, Vol. **19**, No. 3, 409.
22. Huang, He; Wang, Keyu; Wang, Shaojie; Klein, M.T.; W.H. Calkins *ACS Fuel Chem Div Preprints* **40** (3), 485 (1995).
23. Huang, He; Wang, Keyu; Wang, Shaojie; Klein, M.T.; W.H. Calkins paper to be presented in the *Symp. on the Thermal Analytical Techniques*, March 24-29, 1996, in New Orleans.

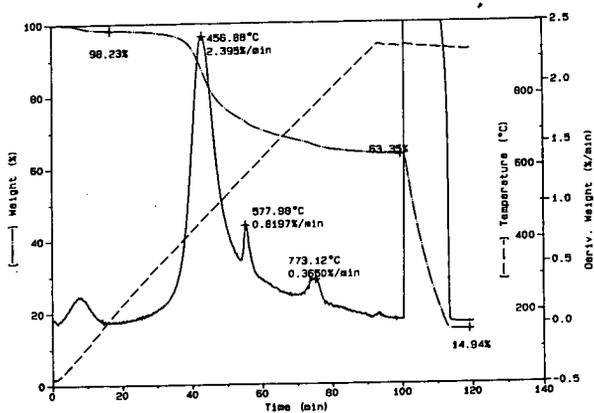


Figure 1 A TG scan of Illinois #6 coal at 10 C/min

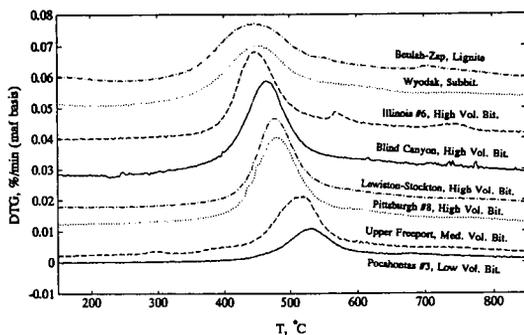


Figure 2 DTG profiles of the eight Argonne coals

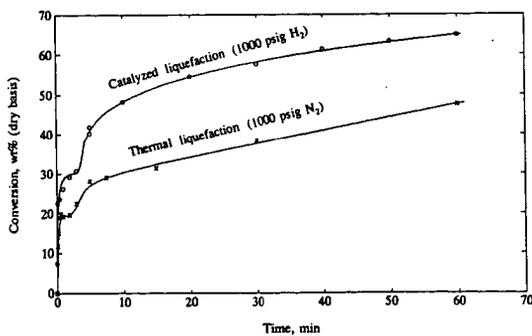


Figure 3 Conversion vs time of the thermal and catalyzed (about 0.9 wt% Mo of sulfided molybdenum naphthenate) liquefaction of Illinois #6

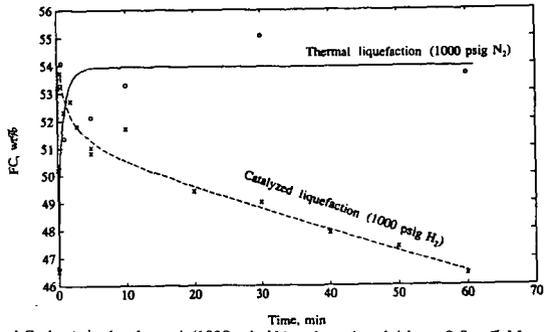


Figure 4 FC (Fixed Carbon) in the thermal (1000 psig N₂) and catalyzed (about 0.9 wt% Mo and 1000 psig H₂) liquefaction residues determined by TGA

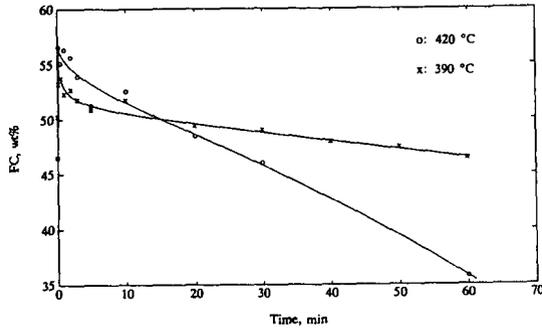


Figure 5 FC (Fixed Carbon) in the catalyzed (about 0.9 wt% Mo) liquefaction residues determined by TGA

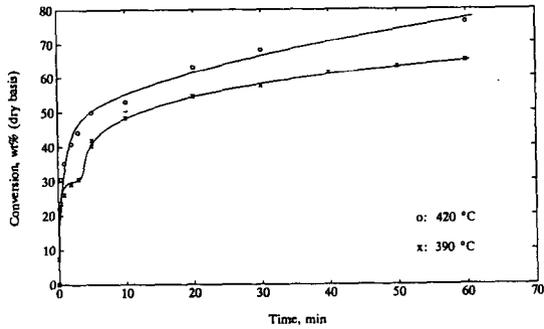


Figure 6 Conversion of the Illinois #6 bituminous in catalyzed (about 0.9 wt% Mo) coal liquefaction under 1000 psig H₂

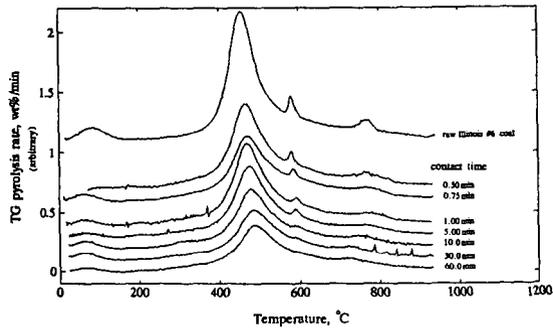


Figure 7 DTG profiles for the liquefaction residues of the Illinois #6 bituminous at the selected contact times

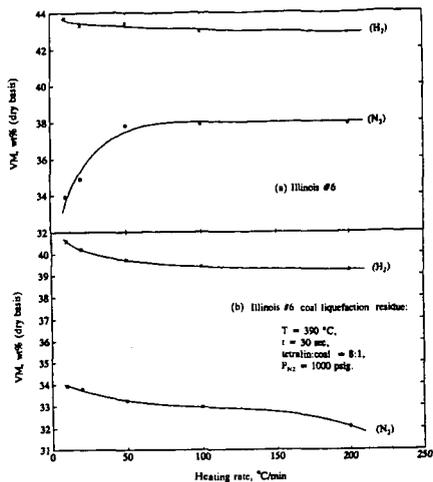


Figure 8 Effect of heating rate and type of purge gas on the VM yields of a). raw Illinois #6 coal and b). its liquefaction residue

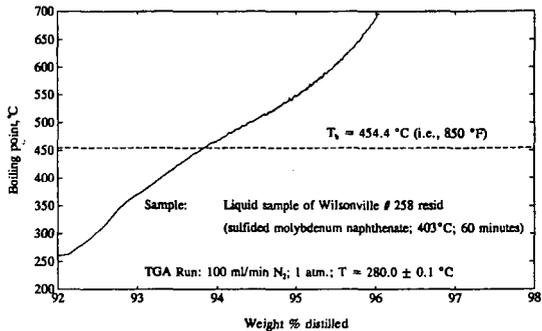


Figure 9 Boiling point distribution of the hydroprocessed reisd liquid determined by SimDis TGA

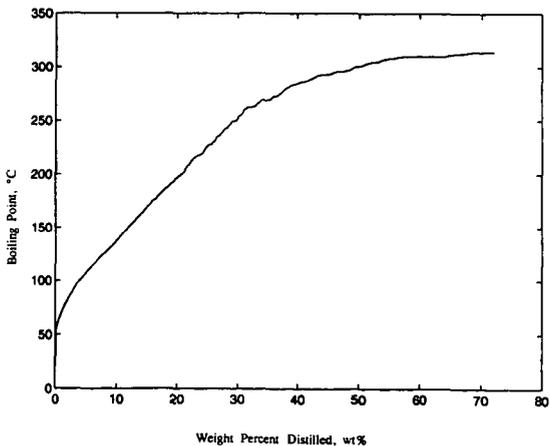


Figure 10 Weight percent distilled vs boiling point of a filtered crude oil determined by a custom built TG for distillation