

Studies in Catalytic Hydroprocessing for Upgrading Coal and Waste-Derived Liquids to Clean Transportation Fuels

H. S. Joo, Keith A. Cain, and James A. Guin

jaguin@eng.auburn.edu

Ph: 334 844-2020 Fax: 334 844-2063

Auburn University

Chemical Engineering Department

Auburn, Alabama 36849

ABSTRACT

A coal-wastes coprocessing liquid, containing 99.6% +205 °C gas oil fraction, was subjected to batch hydrocracking reactions using a commercial NiMo on zeolite-alumina catalyst and gave good conversion to naphtha. The effects of catalyst loading, reaction time, and temperature were investigated. Properties of the upgraded (hydrocracked) liquid including hydrocarbon types, octane numbers, and boiling point distributions were examined and compared with a commercial gasoline. The results indicated good potential for upgrading of the raw coal-wastes coprocessing liquid to higher value products. In addition, the results of similar processing of a residual plastics pyrolysis liquid and a residual tire pyrolysis liquid are examined for comparison. The results indicated that the plastics liquid was easier to upgrade than the coprocessing liquid, while the tire liquid was more difficult to upgrade.

Introduction. Landfill disposal of waste plastics, tires, and other wastes is becoming increasingly costly while the volumes of these wastes are increasing. Most plastics are not readily biodegradable and will remain in the landfill for long periods. Increasing public resistance to the creation of new landfills and higher costs have led to efforts toward finding economically feasible and environmentally acceptable means of plastics recycling. Waste tires are even more bothersome, tending to "float" to the surface in landfills, and to form mosquito breeding locations. Tires also may tend to catch fire during storage. Since federal and state laws are resulting in a significant decrease in the number of sanitary landfills, there is considerable interest in finding new ways of handling these waste materials. Several methods including pyrolysis, gasification, and catalytic liquefaction might deal more effectively with waste plastics than simple mechanical recycling or incineration, since mechanical recycling often yields lower quality products, while incineration produces greenhouse gases. Therefore, there is current interest in producing higher value products from waste materials such as waste plastics, tires, and other items which are currently being landfilled. One possibility is to pyrolyze the waste materials first and produce a liquid which could then be upgraded to more valuable products (1-6). Another possibility is to coprocess these materials with coal using technology developed for the liquefaction of coal itself (7-10). In either approach there is a need to apply catalytic upgrading in order to produce higher value transportation fuels from the raw liquids which are produced in the first stages of the process. Our research seeks to upgrade these primary products to naphtha range fuels. Because coal and coal wastes raw liquids have significant heteroatom contents, high aromaticity, and high molecular weights, hydroprocessing and/or hydrocracking will be required to produce naphtha range products in the transportation fuels range. In this work we report a study of the effects of catalyst loading, temperature, and residence time on the upgrading of several raw liquids including a coal-waste coprocessing liquid, a plastics pyrolysis liquid, and a tire liquid.

Experimental Materials. The coal-wastes coprocessing liquid used as the feed in this study was a vacuum still overheads (VSOH) blend produced by Hydrocarbon Technologies, Inc. in pilot plant Run POC-2 during an 8 day period by coprocessing 12 tons of mixed plastics and 5 tons of crumb rubber from waste tires together with a subbituminous coal from the Black Thunder mine in Wyoming in an approximate 70:30 wt% ratio of coal/wastes [10]. The mixed plastics were designed to simulate a typical post consumer waste and consisted of 50% high density polyethylene, 35% polystyrene, and 15% polyethylene terephthalate. Additional processing details from the POC-2 Run and a process flow diagram showing the location of the VSOH stream are available in the literature [9,10]. The VSOH liquid analyzed as 89.4 wt% C, and 10.2% H. The liquid mostly consists of heavy materials, e.g. 99.6% gas oil (+205 °C) and the H/C atom ratio of 1.37 indicates substantial amounts of aromatic components.

The liquid raw material for the plastics and tire liquid studies was obtained from the Conrad pyrolysis process through the courtesy of Conrad Industries, Inc [3,4]. The plastics liquid was produced by the pyrolysis of a mixed plastics feed consisting of high density polyethylene, polypropylene, and polystyrene [3]. The original pyrolysis liquid was separated by distillation into a light fraction containing 98.9 % naphtha, and a residual fraction containing 71.3 % gas oil. The residual fraction is the feedstock for the upgrading study described in the following work and was 88.7 wt% C, 10.84% H, 0.03% N, 0.14% S. More detailed analysis of this plastics liquid is given by Joo and Guin [11]. The raw tire liquid contained 37% gas oil, and 63% naphtha. This raw liquid was separated (Figure 9) by distillation at 95 °C and 35 mbar into light (94% naphtha, 6% gas oil) and residual (83% gas oil, 17% naphtha) fractions. The residual fraction is 88.77% C, 7.32% H, 0.95% S, 0.15% N, and 2.81% O. and was selected as the feedstock for the upgrading study.

Reaction Procedures and Product Analysis. Reactions were performed in tubing microreactors [11,12].

The catalyst (Akzo KC 2600: 2.6% Ni, 7.0% Mo on zeolite-alumina) was crushed and sieved to -100 mesh before use. Presulfidation using 100% excess S needed for bulk sulfidation to Ni₃S₂ and MoS₂ was performed at 300 °C for 2 h. Reactions were carried out varying catalyst loadings, reaction times and temperatures with 69 atm initial cold hydrogen pressure. Total gas make was calculated by subtraction of the mass of hydrogen remaining after reaction from the total mass of gases. The plastics liquid was also upgraded in continuous tubular fixed bed reactor runs of 100 hr using a sequence of hydrotreating with Criterion 424 NiMo/alumina catalyst followed by hydrocracking with Akzo KC2600. A final gasoline range product was obtained by distillation. Liquid products from the reaction were analyzed by ASTM D2887 GC simulated distillation (SimDist) to obtain the boiling distribution and fractions of naphtha (-205 °C) and gas oil (+205 °C). Proton NMR was performed to estimate the hydrocarbon types and to provide an indication of product quality. From the NMR spectra, the hydrocarbon types including aromatics, paraffins, and olefins, as well as an isoparaffin index, H/C ratio and research octane number (RON) were estimated using literature correlations developed by Myers et al. [13].

Results and Discussion. Figures 1 and 2 show the results of hydrocracking of the coal-wastes and the plastics pyrolysis liquids at different temperatures and catalyst loadings. Gas oil conversions are higher for the plastics liquid, and the reaction conditions are less severe. Effects of temperature and catalyst loading are in the correct directions, and the gas oil conversions approach 100% for the plastics liquid. The corresponding % naphtha in the reaction products is shown in Figures 3 and 4 for the coal-wastes and the plastics liquid, respectively. It can be seen that there is an optimum in the naphtha % due to the tendency to react further to gases, as the severity is increased. Maximum naphtha yield is around 60% for the coal-

waste coprocessing liquid. Comparison of the gas oil conversion and % naphtha for the coal-waste liquid and the plastics liquid is shown in Figures 5-8 as a function of the space time, a combined variable incorporating catalyst loading, reaction time, and liquid loading. It is seen that the plastics liquid is upgraded at less severe conditions than the coal waste liquid, and that the maximum in naphtha % is obtained at a much lower space time at the same temperature. The maximum in % naphtha is around 70% for both liquids. Figure 9 shows the boiling point distribution curve of commercial gasoline, the original tire oil liquid, and its respective light (distillate) and residual fractions. The light fraction, with 94% naphtha, has a boiling point distribution similar to that of commercial gasoline. Figure 10 shows the effect of reaction time on the boiling point distribution for hydrocracking of the residual tire oil. The residual tire oil (feedstock) and the commercial gasoline are included for comparison. As the reaction time is increased, the conversion of gas oil to naphtha increases. The effect of catalyst loading on the boiling point distribution is presented in Figure 11. As the catalyst loading increases, the gas oil conversion becomes greater. Figure 12 shows the effect of temperature on the boiling point distribution. Increases in reaction temperature yield better conversion of gas oil to naphtha, approaching near to the boiling point of commercial gasoline.

Product Quality. An idea of the product quality of some of the upgraded liquids from the hydrocracking reactions was obtained from the NMR analysis [13]. The coal-wastes coprocessing liquid upgraded at 430° C had a gas oil conversion of 96% and a naphtha % of 95%. Using NMR correlations this liquid was 18 vol % aromatics, 78% paraffins, and 4% olefins. The isoparaffin index was 0.82, and estimated RON was 89.4. Elemental analysis gave a H/C ratio of 1.73 and N < 1ppm. The relatively low aromatics content and acceptable RON suggest a beneficial liquid from an environmental viewpoint. A gasoline range distillate product from the sequential hydrotreating/hydrocracking of the plastics liquid gave an aromatics content of 13.8%, 82.5% paraffins, 3.7% olefins, 1.80 H/C, isoparaffin index of 0.84, 89.2 RON, and N < 0.3 ppm, also suggesting favorable properties for transportation fuels.

Acknowledgements: This work was supported by the Department of Energy under the research program of the Consortium for Fossil Fuel Liquefaction Science. Portions of the work were also supported by the NSF EPSCoR program. The authors also wish to thank Conrad Industries, Inc. and Hydrocarbon Technologies, Inc. for supplying the samples used in this work.

References.

1. Marsh, J. A., Cha, C. Y., and Guffey, F. D., *Chem. Eng. Comm.*, **129**, 69 (1994).
2. Williams, S. B. and Taylor, D. T., *Fuel.*, **69** (12), 1474 (1990).
3. Meszaros, M. W., Conrad Advanced Recycling Project, Recycle '94, Davos, Switzerland, 1994.
4. Virgin, B, *Seattle Post-Intelligencer*, July 1, 1993.
5. Kaminsky, W., *Advances in Polymer Technology*, **14** (4), 337 (1995).
6. Kaminsky, W., Schlesselmann, B., and Simon, C. J., *Analytical and Applied Pyrolysis*, **32**, 19 (1995).
7. Taghiei, M. M., Feng, Z., Huggins, F. E., and Huffman, G. P., *Energy & Fuels*, **8** (6), 1228 (1994).
8. Comolli, A. G., Lee, L. K., and Pradhan, V., *ACS Div. Fuel Chem. Prepr.*, **42** (2), 736 (1997).
9. Robbins, G. A., Winschel, R. A., and Burke, F. P. A., *ACS Fuel Chem. Prepr.*, **40** (1), 92 (1995).
10. Pradhan, V. R.; Comolli, A. G.; Lee, L. K.; Stalzer, R., *ACS Fuel Chem. Prepr.*, **40** (1), 82 (1995).
11. Joo, H. S. and Guin, J. A., *Energy & Fuels*, **11** (3), 586 (1997).
12. Joo, H. S. and Guin, J. A., *Fuel Proc. Tech.*, **49**, 137 (1996).
13. Myers, M. E., Jr., Stollsteimer, J., and Wims, A. M., *Anal. Chem.*, **47**, 2301 (1975).

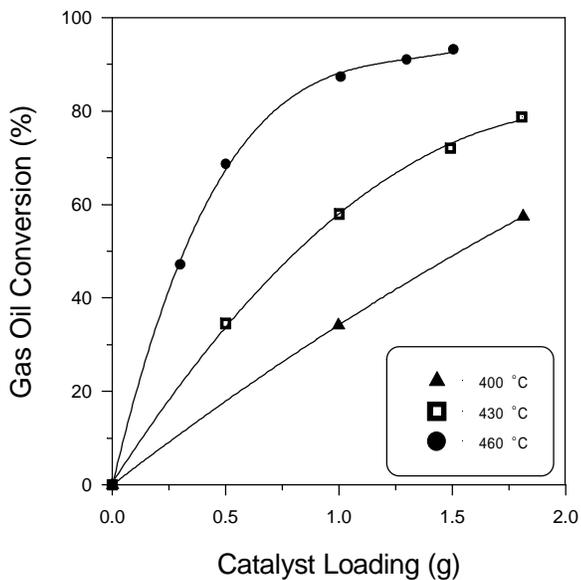


Figure 1 Effect of catalyst loading on gas oil conversion in coal-wastes coprocessing liquid hydrocracking for 1 hr reaction time.

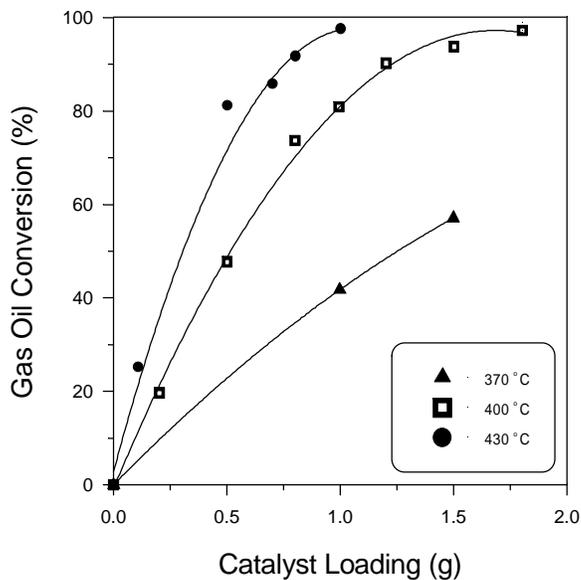


Figure 2 Effect of catalyst loading on gas oil conversion in residual plastics pyrolysis liquid hydrocracking for 0.5 hr reaction time.

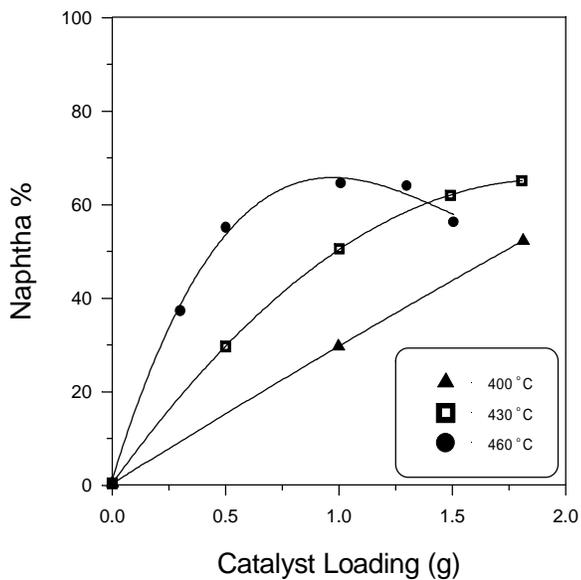


Figure 3 Effect of catalyst loading on percent naphtha in coal-wastes coprocessing liquid hydrocracking for 1 hr reaction time.

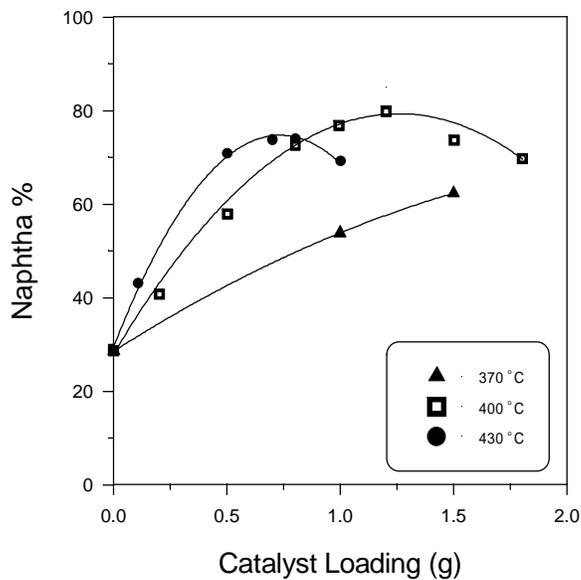


Figure 4 Effect of catalyst loading on percent naphtha in residual plastics pyrolysis liquid hydrocracking for 0.5 hr reaction time.

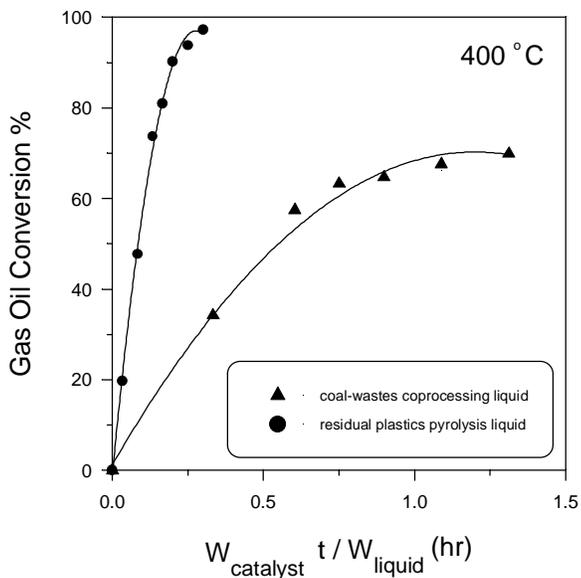


Figure 5 Comparison of gas oil conversion for coal-wastes coprocessing and residual plastics liquids at 400 °C.

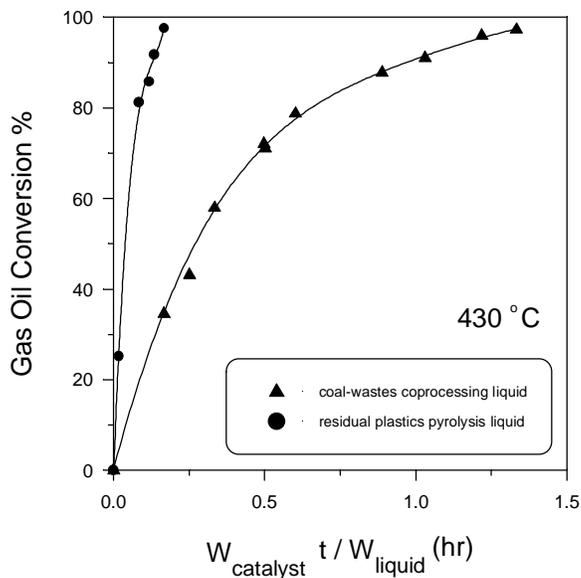


Figure 6 Comparison of gas oil conversion for coal-wastes coprocessing and residual plastics liquids at 430 °C.

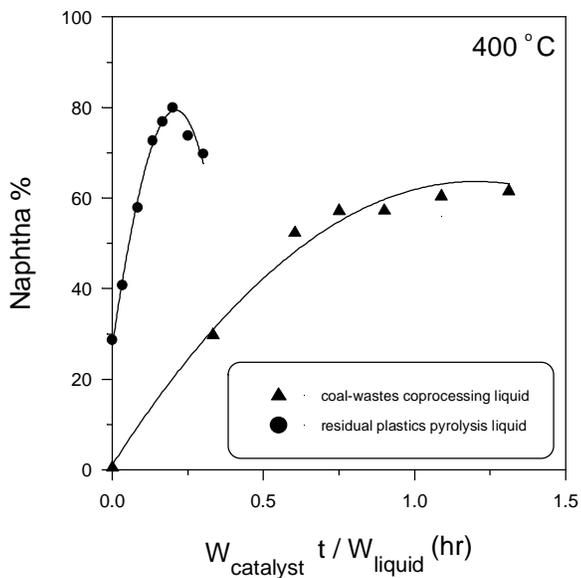


Figure 7 Comparison of percent naphtha for coal-wastes coprocessing and residual plastics liquids at 400 °C.

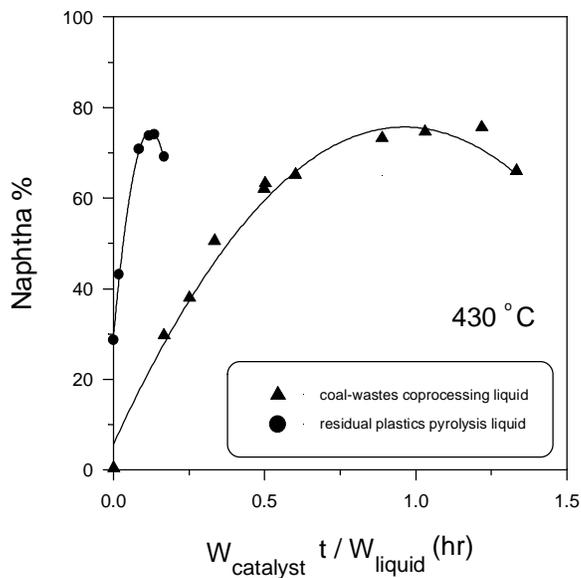


Figure 8 Comparison of percent naphtha for coal-wastes coprocessing and residual plastics liquids at 430 °C.

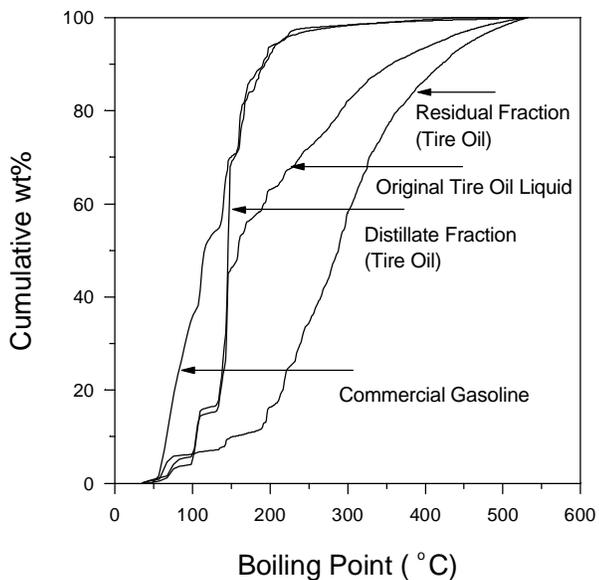


Figure 9 Boiling point distribution curve after distillation of tire oil (95 °C, 35 mbar).

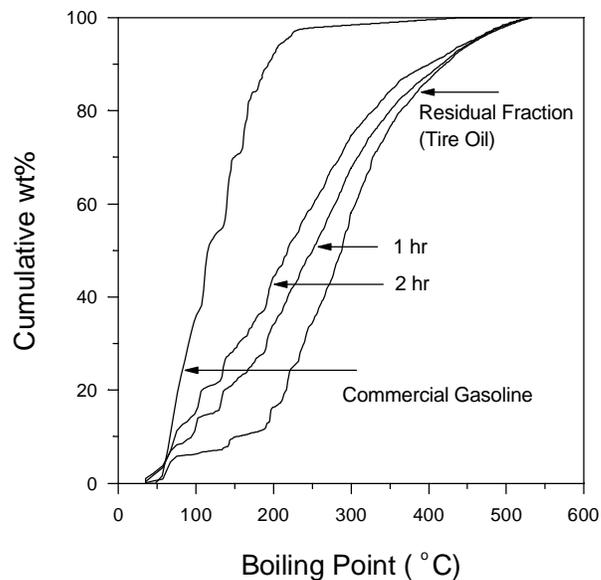


Figure 10 Effect of reaction time on boiling point distribution for hydrocracking of tire oil (430 °C, 1g catalyst).

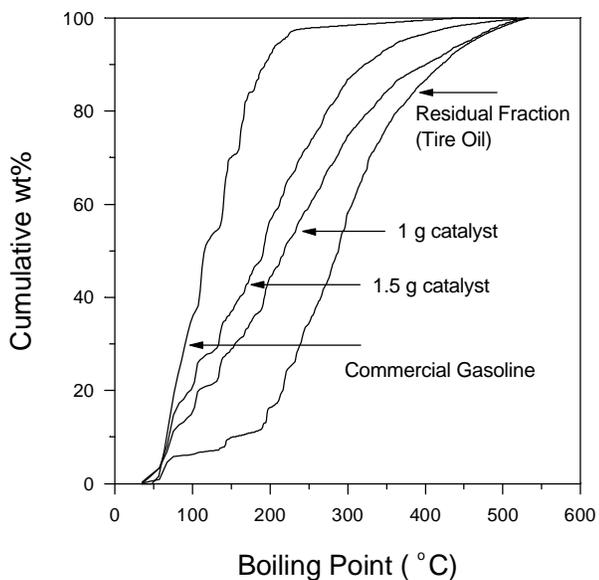


Figure 11 Effect of catalyst loading on boiling point distribution for hydrocracking of tire oil (430 °C, 2 hr reaction time).

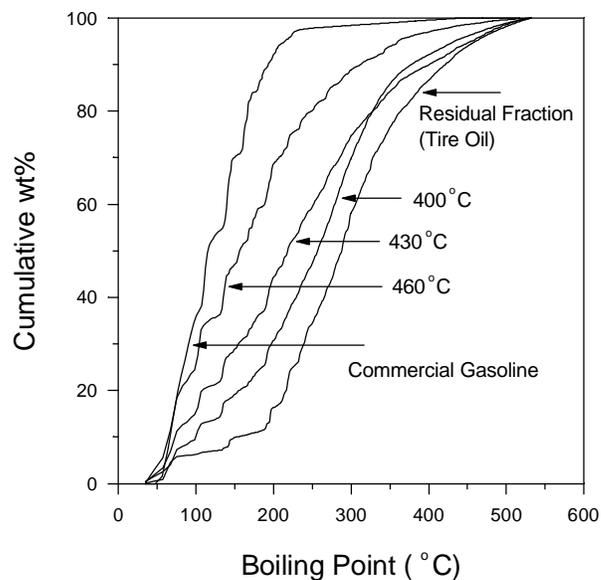


Figure 12 Effect of reaction temperature on boiling point distribution for hydrocracking of tire oil (1g catalyst, 2 hr reaction time).