

# Temperature-Programmed Liquefaction of Low-Rank Coals in H-Donor and Non-Donor Solvents

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## Introduction

U.S. production of low-rank coals including lignite and subbituminous coals has increased tenfold over the last two decades, and production is poised for a further step increase [1]. Recently there has been increasing interest in finding ways to improve conversion of low-rank coals, which are often less readily liquefied than bituminous coals [2]. In coal liquefaction, the thermally derived reactive fragments (radicals) must be stabilized to achieve molecular weight reduction, otherwise they will promptly recombine or crosslink to form more refractory materials [3]. The rate of thermal fragmentation is mainly determined by coal reactivity, temperature, and time, while its balance with the rate of radical capping by hydrogen-donation is a critical factor [3,4]. It is now recognized that low-rank coals are more reactive than had been thought previously, and their conversion in high-severity processes is accompanied by significant retrogressive reactions [5].

Due to the presence of various C-O and C-C bonds in coals, there may be a relatively broader distribution of dissociation energies of bonds connecting the structural units in low-rank coals, as can be visualized from the dissociation energies of various C-O, C-C and C-H bonds that are believed to be relevant to coal and coal conversion processes [6]. The concept of distribution of bond energies for coals is also supported by the results of temperature-programmed pyrolysis (TPP) of coals ranging from brown to bituminous coals [6,7]. TPP data show that more bonds in low-rank coals are thermally broken at lower temperatures as compared to bituminous coals [6]. The question that arises for liquefying low-rank coals is how to balance the rates of bond cleavage with the rates of hydrogen transfer to the radicals. Of some importance to the present work are several recent reports showing that using relatively slow heating rates [3,4,8] is effective for liquefying low-rank coals. In catalytic liquefaction, temperature-staged conditions have been shown to improve coal conversion and oil yields [9-11], even in the aqueous liquefaction system [12].

For a given reaction system, controlling the conditions is important for maximizing the yield and quality of products and minimizing retrogressive reactions. The retrogressive reactions may include the crosslinking of thermally generated radicals and condensation of thermally sensitive compounds. The temperature-programmed liquefaction (TPL) reported here seeks to efficiently liquefy low-rank coals by controlling the rate of pyrolytic cleavage of weak bonds while minimizing the retrogressive crosslinking of radicals and thermally sensitive groups. In preliminary communications, we reported that temperature-programming appears to be promising for more efficient conversion of low-rank coals in tetralin [13,14]. This paper reports on the temperature-programmed and non-programmed liquefaction (N-PL) of a subbituminous coal and a lignite in H-donor and non-donor solvents. Reported separately are the solid-state  $^{13}\text{C}$  NMR and pyrolysis-GC-MS studies of coal structure and the TPL reactions [15], and catalytic TPL of a low-rank coal using dispersed Mo catalyst [16].

## Experimental

The coals used were a Montana subbituminous coal and a Texas lignite obtained from the DOE/Penn State Coal Sample Bank (DECS-9 / PSOC-1546; DECS-1 / PSOC 1538). Table I shows the characteristics of these coals. The coals were recently collected and stored under argon atmosphere in heat-sealed, argon-filled laminated foil bags consisting of three layers (polyethylene plus aluminum foil plus polyethylene) [17]. The coals were crushed to less than 60 mesh and dried in vacuo at 95°C for 2 h (before use) by placing a flask containing the fresh coal into a preheated vacuum oven. Our preliminary data showed that vacuum dried coal gave similar or slightly higher conversion than the fresh coal. The H-donor vehicle used was tetralin, a known H-donor. As non-donor, naphthalene and 1-methylnaphthalene were used. The products from low temperature runs with naphthalene at  $\leq 350^\circ\text{C}$  were rock-like and

difficult to remove from the reactors. However, there were no such experimental problems with 1-methylnaphthalene because it is a liquid. Liquefaction was carried out in 25 mL microautoclaves using 4 g coal (< 60 mesh) and 4 g solvent under 6.9 MPa H<sub>2</sub> using a given temperature program. The liquid and solid products were separated by sequential Soxhlet extraction with hexane, toluene and THF for about 24 h. The THF-insoluble residues were washed with acetone, then with pentane to remove THF completely, and subsequently dried in a vacuum oven at 100°C for over 6 h before weighing. The conversions of coal into THF-solubles were determined from the amount of THF-insoluble residues and are based on the dmmf basis. The yields of preasphaltene (THF soluble but toluene insoluble) and asphaltene (toluene soluble but hexane insoluble) are given as the yields of recovered products, and the yields of oil plus gases are determined by difference between total conversion and the sum of preasphaltene and asphaltene yields.

## Results and Discussion

### Temperature-Programming

Figure 1 shows the reactor heat-up profiles for temperature programmed liquefaction. Although the temperature inside the reactor was not measured, the pressure change of the reactor during the heat-up can give a direct measure of the temperature change. Figure 2 shows the change of sandbath temperature and pressure of the reactor for a TPL run of DECS-9 in tetralin with 6.9 MPa cold H<sub>2</sub> at final temperature of 400°C. The sandbath temperature was controlled manually such that the heating ramp would be the same for all the runs. It can be seen from Figures 1 and 2 that the programming was successfully achieved. The t-p profile in Figure 2 is typical for a thermal run, but a catalytic run shows a different t-p change pattern [6]. No catalyst was used in the present work. The selected temperature program consisted of a low-temperature soak at 200°C for 15 min, programmed heating to a final temperature at about 7°C/min, followed by a 30 minute hold at the final temperature (300, 350, 375, 400, and 425 °C). We expect few chemical reactions to occur at 200°C. The rationale for selecting such a low temperature for soaking is to allow the solvent molecules to penetrate into the interior of coal particle (diffusion and swelling), before they are needed as hydrogen donors for stabilizing the radicals and thermally labile compounds in the subsequent heat-up period and high temperature stage.

### Temperature-Programmed Liquefaction

Figure 3 shows the yields of THF-, toluene- and hexane-soluble products plus gas from duplicate runs of Montana coal, as a function of final TPL temperature. At 300°C, the yield of THF-solubles is only slightly higher than that of the original coal. It should be noted that the low temperature TPL did not cause considerable increase in coal conversion, but did result in some desirable change in coal structure. As shown in Figure 3, the conversion of coal to THF-solubles increased significantly with increasing final temperature from 300 °C (9%) to 400 °C (about 79%), but rose to a much lesser extent from 400 to 425°C (about 82%). On the other hand, the conversion to toluene solubles displayed a monotonic increase from 300 to 425 °C.

Figure 4 shows the product distribution from TPL runs in tetralin as a function of final temperature. It is clear from Figure 4 that from 300 to 350°C, the increase in conversion was due mainly to gains in preasphaltene and asphaltene yields, while the oil yields rose substantially with increasing temperature from 350 to 425°C. It is likely that under the TPL conditions, increasing temperature up to 350°C contributed to cleavage of the weak bonds that released the larger molecules of asphaltene and preasphaltene classes from macromolecular network; increasing temperature from 350 to 400 directly promoted the formation of oil from coal; and further increasing temperature from 400 to 425°C further enhanced oil formation from both coal depolymerization and the thermal cracking of preasphaltene and asphaltene.

We also conducted the control runs under the conventional non-programmed (N-PL) conditions (rapid heat-up from 23°C to reaction temperature in 2-3 minutes) at the temperatures of 350-425°C. Figure 5 compares the TPL and N-PL data for DECS-9 coal in tetralin. As can be seen from Figure 5, relative to N-PL, TPL afforded more preasphaltene at low temperatures between 350-375°C, and more toluene solubles and more oil between 375-425°C. It should be noted that the data in Figure 5 are average of duplicate runs for both TPL and N-PL. The raw data from the duplicate runs show the same trend. For example, the THF conversions from duplicate experiments of N-PL are 70.6 and 72.2% for runs at 400°C, and 75.0, 75.7 and 78.4% for runs at 425°C in tetralin under H<sub>2</sub>. A longer N-PL run at 400°C for extended time period (60 min) only increased the THF conversion by about 2-3 % as compared to the 30 min N-PL run. However, the THF conversions from duplicate TPL runs are 77.0 and 81.4% for TPL at 400°C, and 81.4 and 83.1% for TPL at 425°C. In the case of DECS-1 Texas lignite, TPL runs also gave considerably higher conversions than N-PL runs in tetralin. The average values from duplicate runs of DECS-1 in tetralin are shown in Table 2.

In order to understand the beneficial effects of TPL in H-donor tetralin, we also conducted both TPL and N-PL runs in

non-donor solvents. The data in Table 2 and Table 3 shows that temperature-programming in a non-donor solvent such as naphthalene or 1-methylnaphthalene does not appear to have any significant impact on coal conversion and product distribution. This indicates that beneficial effects of TPL as compared to N-PL in tetralin solvent are closely associated with hydrogen transfer from tetralin.

The above results demonstrated that in the presence of H-donor solvent, TPL can afford considerably higher conversion than the conventional run at the same or even higher final temperatures. This comparison clearly showed that the programmed heat-up is superior to the rapid heat-up for conversion of the low-rank coals in tetralin under H<sub>2</sub>, although it is known that in coal pyrolysis ultrarapid heating increases tar yields [18]. These results indicate that the temperature-programming is a promising approach for converting low-rank coal in H-donor solvent, and further improvement may be achieved by finding the optimum program and by using a catalyst. In fact, we also demonstrated that catalytic TPL of DECS-9 is superior to N-PL in the presence of a dispersed Mo catalyst and a process solvent which has much lower H-donating ability compared to tetralin [16]. Analytical characterization of the residues using CPMAS <sup>13</sup>C NMR and pyrolysis-GC-MS [15] points to the progressive loss of oxygen functional groups and aliphatic species from the macromolecular network of the subbituminous coal during its depolymerization in tetralin under TPL conditions. The higher conversions in TPL runs (relative to the conventional runs in tetralin) suggest that the removal of carboxylic and catecholic groups from the coal during the programmed heat-up in tetralin may have contributed to minimizing the retrogressive crosslinking at higher temperatures.

### Mechanistic Considerations

Comparative examination between the TPL and N-PL runs using different solvents established that the beneficial effects of temperature-programming in tetralin are not due to thermal treatment but are closely associated with low temperature hydrogen-transfer during programmed heat-up. Although H-transfer is a chemical process, both the physical and chemical mechanisms can be responsible for the desirable effects of TPL as compared to N-PL in tetralin. Our initial idea in designing the temperature program was to meet the physical as well as chemical requirements for conversion of coals which are macromolecular in chemical nature but are microporous in physical nature. The rationale of selecting a low temperature soak is associated with the characteristics of coal pore structure. A large part of pore volume of low-rank coals is located in mesopores (20-500 Å in diameter) and macropores (>500 Å). However, most of the surface area of coals is enclosed in the micropores (<20 Å); hence rates of reaction are limited by rates of diffusion through the micropores [19,20]. Spears et al. [20] reported that the micropore walls contain polar functional groups, and their abundance is higher for low-rank coals. It is considered that soak at 200°C for 15 min will facilitate the diffusion of tetralin into the micropores (< 20 Å) and smaller mesopores (>20 Å). Also, possibility exists that tetralin could induce swelling at 200°C which may open up some pores that are solvent-inaccessible at room temperature. However, such physical effects would be smaller for liquefaction of bituminous coals.

The chemically beneficial effect of TPL compared to N-PL in H-donor lies in the programmed heat-up. The H-transfer from H-donor could stabilize the thermally derived radicals and thermally sensitive groups. Because of the bond dissociation energy distribution, one could selectively break certain bonds at certain temperature range by using temperature programming, which would provide time for radical to abstract H from H-donor. Low-rank coals are characterized by low aromaticities and high oxygen functionalities [21]. Suuberg et al. [22], Solomon et al. [18] and Lynch et al. [23] have indicated that during coal pyrolysis, decarboxylation is accompanied by crosslinking reactions and the formation of CO<sub>2</sub>. McMillen et al. [24] have provided some insights into the retrogressive reactions involving polyhydroxy structures. It is likely that the retrogressive reactions occurring during liquefaction of low-rank coals under conventional high-severity conditions are, at least in part, associated with the reactions of their oxygen functional groups. It seems possible from comparative examination of the coal conversion data that the TPL conditions may facilitate the reduction of crosslinking reactions of the thermally sensitive groups such as oxygen-functional groups at low temperatures in H-donor. Both the present and previous results [3,4,8] strongly suggest that very fast heating would result in too fast a thermal fragmentation of low-rank coals at high temperatures to be balanced by H-donation, which consequently leads to enhanced retrogressive reactions.

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**Table 1.** Representative Analyses of DOE / Penn State Coal Samples

Sample No.	DECS-9 or PSOC 1546	DECS-1 or PSOC 1538
<b>Proximate (wt%)</b>		
Volatile Matter	33.5 (47.1) <sup>a</sup>	33.2 (55.5) <sup>a</sup>
Fixed Carbon	37.1 (52.9) <sup>a</sup>	25.8 (44.5) <sup>a</sup>
Moisture	24.6	30.0
Ash	4.8	11.1
<b>Ultimate (wt%, dmmf)</b>		
Carbon	76.1	76.1
Hydrogen	5.1	5.5
Nitrogen	0.9	1.5
Organic Sulfur	0.3	1.1
Oxygen (by diff)	17.6	15.8
<b>Source &amp; Rank</b>		
State	Montana	Texas
County	Bighorn	Freestone
City	Decker	Fairfield
Seam	Dietz	Bottom
Age of Seam	Paleo	Eocene
ASTM Rank	Subbit B	Lig A / Sub C
Sampling Date	6/12/90	12/1/89

a) On a dry, mineral matter free (dmmf) basis.

**Table 2.** Temperature-Programmed (TPL) and Non-programmed Liquefaction (N-PL) with H-Donor Teralin and Non-donor 1-Methylnaphthalene (1-MN) Solvents at 400 °C for 30 min

Coal	DECS-9	DECS-9	DECS-1	DECS-1	DECS-9	DECS-9
	Mont Sub	Mont Sub	Texas Lig	Texas Lig	Mont Sub	Mont Sub
	TPL	N-PL	TPL	N-PL	TPL	N-PL
Solvent	Tetralin	Tetralin	Tetralin	Tetralin	1-MN	1-MN
<b>Prod. dmmf wt%</b>						
THF-Conv <sup>a</sup>	79.2	71.4	78.0	69.8	34.1	32.2
Tolue-Conv <sup>b</sup>	55.5	50.1	66.1	58.0	27.1	25.4
Oil + Gas	34.4	29.4	48.5	45.1	18.9	16.0
Asphaltene	21.1	20.6	17.5	12.9	8.2	9.4
Preasphaltene	23.7	21.4	11.9	11.8	7.0	6.8

a-b) Total conversion to a) THF-solubles and b) toluene-solubles plus gas.

**Table 3.** Temperature-Programmed (TPL) and Non-programmed Liquefaction (N-PL) with H-Donor Teralin and Non-donor Naphthalene Solvents at 350 °C for 30 min

Coal	DECS-9	DECS-9	DECS-9	DECS-9
	Mont Sub	Mont Sub	Mont Sub	Mont Sub
	TPL	N-PL	TPL	N-PL
Solvent	Tetralin	Tetralin	Naphthalene	Naphthalene
<b>Prod. dmmf wt%</b>				
THF-Conv <sup>a</sup>	42.0	31.9	21.3	21.4
Tolue-Conv <sup>b</sup>	19.2	17.0	13.7	14.2
Oil + Gas	2.7	4.0	9.3	7.9
Asphaltene	16.5	13.0	4.4	6.3
Preasphaltene	22.8	14.9	7.6	7.2

a-b) Total conversion to a) THF-solubles and b) toluene-solubles plus gas.

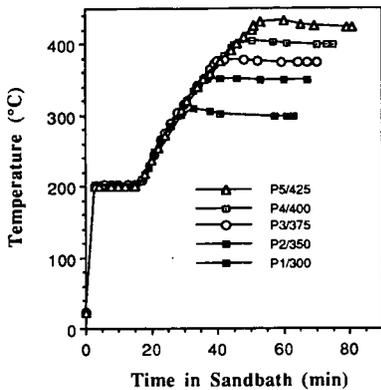


Figure 1. Temperature programs examined in TPL of DECS-9 coal.

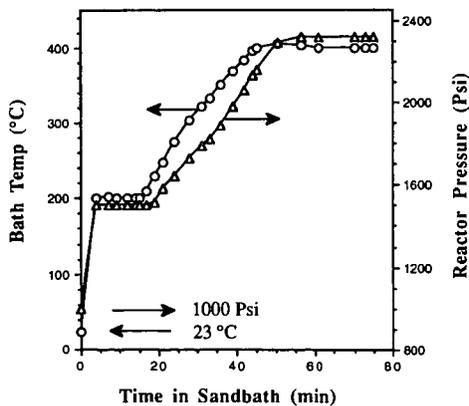


Figure 2. Typical temperature-pressure profile during programmed heat-up and holding for non-catalytic TPL of DECS-9 coal in tetralin at a final temperature of 400 °C.

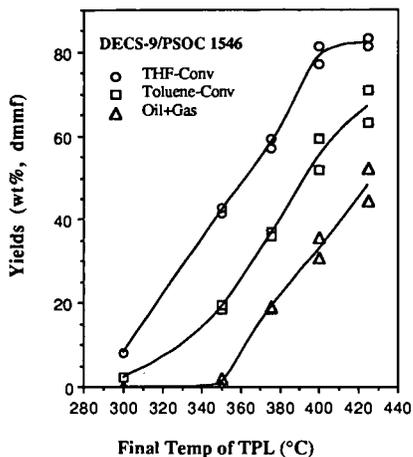


Figure 3. Relationship between final temperature of TPL and coal conversion to THF-, toluene- and hexane-solubles plus gases.

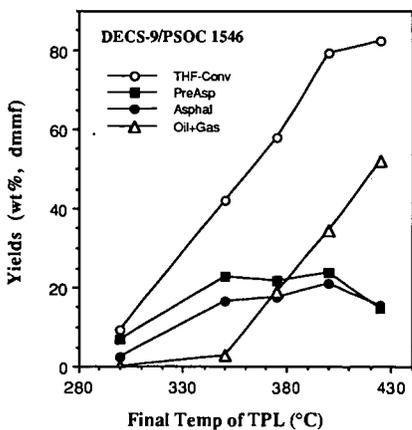


Figure 4. Product distribution from TPL of DECS-9 in tetralin at different final temperatures ranging from 300 to 425°C.

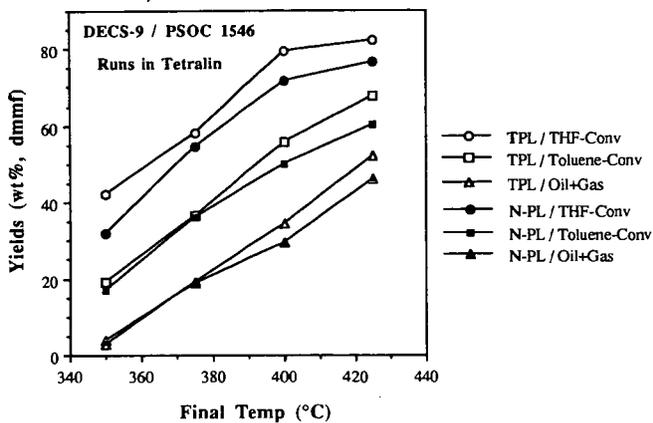


Figure 5. Comparison between temperature-programmed (TPL) and non-programmed (N-PL) runs of DECS-9 coal in tetralin solvent.