The Use of Mixed Pyrrhotite/Pyrite Catalysts for Co-Liquefaction of Coal and Waste Rubber Tires

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OBJECTIVES

The overall objective of this research program is to determine the optimum processing conditions for tire/coal co-liquefaction. The catalysts used will be our ferric-sulfide-based materials, as well as promising catalysts from other consortium laboratories. The intent here is to achieve the maximum coal+tire conversion at the mildest conditions of temperature and pressure. Specific objectives include an investigation of the effects of time, temperature, pressure, catalyst and co-solvent on the conversion and product slate of the co-liquefaction.

ACCOMPLISHMENTS AND CONCLUSIONS

Introduction

There is now a growing body of research attesting to the technological possibility [1,2] and economic feasibility [3] of co-liquefying waste tire material with coal. While other waste materials such as plastics may show greater short-term viability for co-liquefaction, the long-term advantages of tires as a feedstock include greater homogeneity from type to type, and lower amounts of environmentally flagged constituents such as chlorides.

The majority of the coal samples has been from DECS-6, which is a high-volatile A bituminous coal from the Blind Canyon seam in Utah. Other coals used include DECS-24 (Illinois number 6; bituminous, high-volatile C) and DECS-26 (Wyodak; sub-bituminous B). All coals were sized to -60 mesh. The proximate and ultimate analyses of the coal samples are given in Table I.

Three different tire materials have been tested. The first samples were prepared from a Goodyear Invicta tire, recycled in-house at WVU (Tire-1). Another sample, obtained from the University of Utah, was a recycled tire ground to -30 mesh (Tire-2). The third sample (Tire-3) consists of truck tire, also obtained from the University of Utah. Tire sample sizes were -30 mesh. The majority of the tire samples used this year have been from Tire-2. Analyses of all the tire samples are also given in Table I.

The catalyst tested in this work is based on ferric sulfide as a precursor. Disproportionation of the ferric sulfide results in an intimate mixture of pyrrhotite and pyrite (and elemental sulfur), and this has been shown to be a very effective catalyst in coal liquefaction [4-6].

For all the data reported below, total conversion was based on the measurement of tetrahydrofuran (THF)-insoluble matter. The asphaltene+preasphaltene yield was found from the measurement of (THF-soluble but) hexane-insoluble matter. For most runs, the gas fraction was measured separately, using gas chromatography. The oil fraction was found by difference. In the case of co-liquefaction experiments, the results are reported on a "coal-alone" basis, *i.e.*, with the effect of the tire subtracted proportionately. This procedure allows us to compare the results of experiments with coal alone directly with the results of coal-plus-tire experiments.

Some of our work in this area has been described in the literature [2,4,7]. Preliminary baseline runs with Tire-1 and DECS-24 indicate:

(1) the organic matter in the tire is almost completely converted to oils, at least after 0.5h at 400°C and 1000 psig (cold) H_2;

(2) there is little effect of H_2 pressure on tire liquefaction;

(3) co-liquefaction of tire and coal results in an increase in asphaltenes produced, with oil and gas yields being unchanged;

(4) co-liquefaction yields depend upon the temperature and the tire-to-coal ratio, but there is little dependence upon the hydrogen pressure, at least after around 500 psi(cold);

(5) the synergism between coal and tire probably arises when the radicals generated from the coal combine with C_{2+} fragments from the tire to produce asphaltenic fractions rather than with other coal radicals to form condensation products;

(6) untreated residue from the tire has no special effect on the conversion or product slate after co-liquefaction

(7) ferric-sulfide-based catalysts generated *in-situ* in the coal can improve conversions and oil yields during co-liquefaction, at loadings as low as 0.5wt% of the coal.

Results of three investigations are reported here. In the first, a statistical design was used so that temperature, pressure and time of liquefaction, coal type, and catalyst loading could be systematically altered over relatively narrow ranges. In the second, a particular coal-tire system was used, and the effects of temperature and tire-to-coal ratio were more extensively investigated. In the third, preliminary work has been started on the pretreatment of the tire residue for use as a possible catalyst during coal liquiefaction.

Effect of Experimental Conditions on Co-liquefaction of a Spectrum of Tire-Coal Pairs

A Box-Behnken statistical design was used. Reactor temperatures ranged from 350-450°C, reaction times from 0.25-1h, and hot hydrogen pressures from 0-2000psi. The total pressure (hot basis) was kept constant at 2000psi by adding helium as appropriate. No additional solvent was added in this work. Tire-2 was used in this portion of the work. Different coals were used by the two investigators who worked on this portion of the project: one worked with DECS-24 and the other with DECS-26, and both worked with DECS-6 coal. Results were obtained for the total conversion (X), and the yields of asphaltene+preasphaltene (A+P), oil (O) and gas (G). A polynomial fitting procedure was used, with the polynomials including terms of up to second order, including cross terms. The expressions were centered at 400°C, 0.5h, and 1000 psi(hot), approximately the midpoint of the respective ranges. Terms deemed to be statistically insignificant (t ratio less than 2) were dropped.

Results with the common coal alone and the tire alone for the two investigators are summarized in Table II. Even though the actual coefficients in the polynomials of Table II are not identical between the two investigators, the two sets of experimental values (not shown) agree to within 2 percentage points, and the predicted values agree with the corresponding experimental values for each investigator to within 2 percentage points. Hence the results for the two investigators can be considered to be reproducible, and we can therefore compare the results using DECS-6, DECS-24 and DECS-26 with the tire, as obtained by the two investigators.

For DECS-6, the coefficients from Table II indicate that conversion is highly dependent upon temperature, and moderately dependent upon hydrogen pressure. Reaction time only exhibits a slight influence upon conversion. Gas yield is also highly dependent upon temperature, with moderate dependencies upon both pressure and time. Oil yields are highly dependent upon temperature, and moderately dependent upon time. The hydrogen pressure has virtually no effect upon oil production. A+P yields show a reasonable dependence upon all three parameters, with temperature being slightly more important. Based on the coefficients of Table II, the surfaces of Figure 1 show the effect of temperature, time and pressure on the overall conversion, while the surfaces of Figure 2 show the effects of temperature and time on the conversion and product yield for the highest hydrogen pressure.

For Tire-2 alone, the corresponding surfaces are shown in Figure 3. The conversion is highly dependent upon temperature and slightly dependent upon time. Gas yield is highly dependent upon temperature and time. Oil yields seem to follow the same general trend as conversion; a high dependence upon temperature with a slight dependence upon time. A+P yields were too small to be modeled with much confidence. The effect of pressure is not explicitly shown in Figure 3. While conversion is relatively independent of hydrogen pressure, this effect is somewhat more pronounced for oil production, and somewhat greater for gas production.

For DECS-26 coal, Figure 4, conversion shows a strong dependence upon hydrogen pressure and only a moderate dependence upon temperature. A slight dependence upon reaction time is observed. Gas yield exhibits a strong dependence upon temperature, with moderate dependencies upon both pressure and time. Oil yields exhibit a strong dependence upon temperature, moderate dependence upon pressure, and slight dependence upon time. A+P yields show approximately equal dependence upon both temperature and pressure. Reaction time has almost no significance in asphaltene and preasphaltene production.

A quantitative analysis of the results with the coals and the tire (each alone) lead to the following "optimum" conditions for each: 400°C, 1h, 2000 psi for DECS-6; 450°C, 1h, 2000 psi for DECS-26; 450°C, 1h, 1500 psi for DECS-24; and 400°C, 0.5h, 2000 psi for Tire-2. (The values above are the rounded-off values of the parameters. The values corresponding to maximum conversion, maximum oil yield, etc. can be predicted using the polynomial expressions analogous to that in Table II. The parameter values above correspond to conversions and yields within expected error bars of the predicted maximum values.) Co-liquefaction experiments were run under these conditions at values of tire-to-coal ratios, R_{TC}, ranging from 0 to 2. As noted earlier, the results are reported on a "coal-alone" basis.

For DECS-26 and Tire-2, the conversion increases with R_{TC} upto the maximum value used. When DECS-6 coal is used, however, the conversion increases when R_{TC} is equal to 1, but then decreases at $R_{TC} = 2$. In all cases, the incremental conversion corresponds mostly to an increase in the A+P yield. Oil yields are affected slightly. Gas yields are virtually unchanged.

Preliminary results with the ferric-sulfide-based, *in-situ* impregnated catalyst have also been obtained on the DECS-6 and DECS-26 coals with Tire-2. The catalytic runs were made both at a low temperature (350°C) and at the "optimum" temperature for the corresponding coal. The reaction time and hydrogen pressure were kept at the maximum value of their respective ranges. Results (on a "coal-alone" basis) using the coal, catalyst and tire with $R_{TC} = 1$ are compared with those using the coal and catalyst, and those using the coal alone. At the low temperature, the catalyst has little effect on the coal alone. However, at the higher temperature, the catalyst increases the conversion dramatically. For DECS-26, this is due to increasing yields of A+P and gas; for DECS-6, this corresponds to increasing A+P alone. When the tire is added to catalyst-impregnated DECS-26, the conversion increases by approximately 7 percentage points. Interestingly, this is due to changes in oil yield and gas yield. When the tire is added to the impregnated DECS-6 coal, the conversion is 7 percentage points lower than that with the catalyst-impregnated coal alone. However, the conversion is 20 percentage points higher than that with the (unimpregnated) coal plus tire. Clearly the catalyst has a considerable effect, but the effect is somewhat attenuated by the presence of the tire. The product distribution from the impregnated coal-plus-catalyst run is also interesting: the decrease in conversion is almost entirely at the expense of the gas yield. These results are consistent with our preliminary findings regarding the role of the tire and the role of the catalyst in the co-liquefaction.

Effect of Temperature, Tire-to-Coal Ratio, and Catalyst Preparation for a Given Tire-Coal Pair

Results using (uncatalyzed) DECS-6 coal, Tire-2, and mixtures at various values of R_{TC} and various temperatures are summarized in Table III. The conversion of tire increases from 66.5 wt% at 375°C to around 69 wt% at 400 and 425°C. The product is mainly oil. The amount of gaseous product is between 2-4 wt%. The conversion of coal also increases with temperature, from about 27 wt% at 375°C to 37% at 425°C. The increase in conversion is mostly accompanied by an increase in the oil yield, which is nearly double at 425°C (21.5%) than at 375°C (10.2%).

With the addition of tire, the conversion of coal increases, indicating a synergistic effect of tire. The increase was found to be dependent on both R_{TC} and temperature. At 375 and 400°C, the conversion of coal increases continuously with the increase in R_{TC}. However, at 425°C, the conversion is maximum (50%) when $R_{TC} = 1$. This work, though performed independently of work reported in the previous section, is consistent with the results reported therein.

The effect of catalyst preparation conditions on its activity was also studied. Specifically, Table IV shows the effect of drying temperature on the product slate at 400°C for R_{TC} values of 1 and 2, as well as for the corresponding feed components by themselves. In all cases, the catalyst loading was fixed at 1.67% of the coal. In the coal-alone runs, the conversion of coal decreases slightly as the drying temperature is increased. However, in the co-liquefaction runs, a drying temperature of 150°C is generally beneficial to the activity of the catalyst. The results indicate that the addition of tire is detrimental to the activity of the catalyst, especially when the drying temperature is below 118°C or when $R_{TC} = 2$. Catalysts used below were dried at 150°C.

Table V shows the effect of liquefaction temperature on the conversion and product yields of catalyzed co-liquefaction. As expected, the conversion of coal in coal-alone runs increases with increase in temperature. The yield of asphaltenes is maximum (40.9%) at 400°C, whereas the yield of oil is maximum (28.3%) at 425°C. This indicates that the asphaltenes are probably converted to oil at 425°C. In the co-liquefaction runs, the conversion of coal is maximum at $R_{TC} = 1$, after which it either decreases or, at the highest temperature, levels off. At all temperatures, oil yields in co-liquefaction runs are lower than those in coal-alone runs.

As mentioned earlier, the catalyst loading used has been 1.67%, based on coal. However, with the addition of tire to the catalyst-impregnated coal, the total amount of catalyst in the reacting system decreases. In order to study the effect of the catalyst, runs were carried out in which the total amount of catalyst (*i.e.*, based on coal-plus-tire) was kept constant while R_{TC} was varied. This was done by first impregnating coal with catalyst to a loading of 5%, based on coal. Then, appropriate amounts of un-impregnated ("raw") coal and/or tire were added such that the catalyst loading was always 1.67%, based on coal-plus-tire, while R_{TC} was varied. (Earlier results reported in [2] indicate that mixing our catalyst-impregnated coal with "raw" coal results in liquefaction yields undistinguishable from runs where the average amount of catalyst is impregnated on the entire amount of coal.) The results are presented in Table VI. The conversion of coal increases from 65%, in the absence of tire, to 75% in the presence of tire, independent of R_{TC}. The increase in conversion is tied to the increase in the yield of asphaltenes. The results are consistent with our earlier hypothesis on the interaction of the catalyst with tire. When the total amount of catalyst is kept the same, the conversion and product slate are independent of R_{TC}.

Using the Tire Residue as a Reaction Enhancer for Coal Liquefaction

As noted earlier, the residue after liquefaction of tire alone has no particular beneficial effect on coal liquefaction. This was demonstrated [2] by comparing the results of liquefaction of coal plus tire with the results when the feed consisted of coal and the liquid products from tire liquefaction (*i.e.*, when the residue was absent); no significant change could be seen. However, Consortium colleagues at Auburn and elsewhere have reported (*e.g.*, [8]) that the tire residue, when pretreated, may have catalytic activity towards coal liquefaction. Preliminary runs were made with tire residue obtained in two ways in this work: in an autoclave, and in the conventional tubing-bomb reactor (TBR) used for the other liquefactions. The first method has the potential of generating larger amounts of residue in one run, if scale-up problems can be overcome. In both cases, the tire was reacted under standard liquefaction conditions (SLC): 400°C, 1000 psi H_2 pressure, 0.5h. The product was extracted with THF to obtain the THF-insoluble material as residue. The residue obtained in each case was heat treated at 560°C for 1h under N_2.

The reactivity of the residue itself was checked by heating it under SLC. The amount of THF-soluble material ("conversion") after this process was below 1%. This indicates that the residue is stable under these conditions, *i.e.*, that all reactive species have been removed.

The tire residue, obtained by each of the two methods above, was used in the liquefaction of DECS-6 coal. The liquefaction was also performed under SLC. The residue-to-coal ratio was 0.33, much higher than the loading of the iron-based catalyst above, to ensure that relatively small changes in conversions could be detected.

With the tire residue obtained from the autoclave, the conversion of coal increased from around 35% (without residue) to 48%. The conversion of coal also increased when it was liquefied with the tire residue from the TBR. However, the increase in the latter case was much higher than with the autoclave residue. The exact reason for this difference is not clear. One possibility is that the TBR residue may have been contaminated with the copper anti-sieze lubricant during the washing of the TBR with THF. No such lubricant was used with the autoclave. Alternatively, the different characteristics for heat and mass transfer in the two reactors may be the cause of the different effects. Clearly, further work is needed.

The activity of the residue was also found to depend on the treatment time at 560°C. For example, when the treatment time of the autoclave product was increased to 4h, the conversion of coal increased to 57%. The increase in conversion was mostly accompanied by an increase in the yield of asphaltenes.

Conclusions

Optimum processing conditions for co-liquefaction (temperature, pressure, R_{TC}, catalyst loading) depend upon the nature of the coal and the tire used.

The ferric-sulfide-based, *in-situ* impregnated catalyst improves the coal conversion, but the effect is attenuated by the presence of the tire.

The residue from the tire, if suitably pretreated, may increase liquefaction conversions.

PLANS

The product slate from our co-liquefaction runs has not been adequately characterized to date, except for solubility-based separation into asphaltenes+preasphaltenes, oils and gases. We expect to be working with other members of the Consortium to characterize these products better. We plan to tie the product quality to coliquefaction conditions.

The use of waste oil as a co-solvent in the co-liquefaction of tires and coal presents opportunities both for the removal of an additional waste and for improving liquefaction yields.

We plan to study the effect of pretreatment of the tire residue on its ability to enhance the co-liquefaction reaction. In particular, the problems associated with scale-up of the generation of the residue need to be resolved.

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Table I

Proximate and Ultimate Analyses of Coal and Tires Used.

Coal analyses from Galbraith Laboratories; Tire analyses from Penn State Coal Bank

SAMPLE	H_2O %	ASH %dry	VOLATILE MATTER %daf	FIXED CARBON %daf	C %daf	H %daf	N %daf	S %daf
TIRE-1	0.3	4.7	67.1	32.9	84.3	7.4	<0.5	1.6
TIRE-2	0.4	8.1	71.0	29.0	79.7	7.5	<0.5	1.7
TIRE-3	0.5	7.3	67.1	32.9	81.8	7.3	<0.5	1.4
DECS-6	1.8	6.3	49.0	51.0	81.9	6.3	1.5	0.9
DECS-26	0.8	6.6	48.5	51.5	75.5	6.1	1.0	0.5
DECS-24	---	13.4	47.0	53.0	76.3	5.3	1.3	6.4

TABLE II

Coefficients for X, AP, O, G from two investigators using DECS-6 coal. Coefficients correspond to
$Y = A_0 + A_T*T + A_t*t + A_P*P + A_{Tt}*T*t + A_{TP}*T*P + A_{tP}*t*P + A_{TT}*T^2 + A_{tt}*t^2 + A_{PP}*P^2$
where T = (temperature [°C] - 400)/400; t = (time [h] - 0.5)/0.5; P = (H_2 pressure [psig hot] - 1000)/1000
"---" indicates that the term is not statistically significant

Y	A_0	A_T	A_t	A_P	A_{Tt}	A_{TP}	A_{tP}	A_{TT}	A_{tt}	A_{PP}
X (BB)	31.8	7.93	1.75	2.79	-0.837	1.38	2.64	-6.03	---	-1.58
(FH)	32.5	6.09	0.649	3.2	-1.25	---	2.6	-6.22	---	1.04
A+P (BB)	12.7	-2.92	-2.05	1.76	-1.33	0.745	---	-5.8	---	---
(FH)	11.4	-3.72	-2.14	1.88	---	1.23	---	---	-4.85	---
O (BB)	14.7	6.13	2.33	---	---	---	2.52	-2.18	---	---
(FH)	18.3	4.83	1.36	---	---	-1.328	2.45	-3.54	---	---
G (BB)	3.41	4.78	1.93	0.781	1.13	1.21	---	2.01	-0.756	---
(FH)	2.95	4.26	2.29	0.445	1.22	1.39	-0.891	2.79	1.68	1.01

TABLE III

Effect of Liquefaction Temperature (T) and Tire-to-Coal Ratio (R_{TC}) on Product Yields
Other Liquefaction Conditions: 1000 psi(cold) H_2, 0.5h.
Results for tire-coal mixtures on "coal-alone" basis.

	TIRE-2	DECS-6	R_{TC} = 1	R_{TC} = 2
T = 375°C				
X	66.5	27.1	34.1	36.6
A+P	1.1	15.8	25.1	29.8
O	63.2	10.2	7.2	4.3
G	2.2	1.1	1.8	2.5
T = 400°C				
X	69.1	31.4	43.8	44.7
A+P	1.1	15.5	31.8	35.7
O	64.7	14.9	8.2	4.3
G	3.3	2.0	3.8	4.7
T = 425°C				
X	69.5	37.2	50.1	49.8
A+P	1.1	11.0	23.6	28.7
O	64.4	21.5	20.0	12.9
G	4.0	4.7	6.5	8.2

TABLE IV

Effect of Catalyst Drying Temperature on Product Yields
Liquefaction Temperature = 400°C; Other Parameters as in Table III

	DRYING TEMPERATURE, °C			
	25	92	118	150
DECS-6				
X	69.1	67.5	64.9	62.4
A+P	43.6	46.5	42.6	40.9
O	22.3	18.5	20.3	18.8
G	3.3	2.5	2.1	2.8
$R_{TC} = 1$				
X	68.1	61.8	66.4	66.0
A+P	47.8	43.3	44.1	50.2
O	16.2	15.3	20.0	13.4
G	4.2	3.2	2.3	2.4
$R_{TC} = 2$				
X	---	49.8	60.7	60.7
A+P	---	38.4	46.9	46.9
O	---	8.1	10.7	10.7
G	---	3.3	3.2	3.2

TABLE V

Catalytic Liquefaction of DECS-6 Coal and Tire-Coal Mixtures. Catalyst dried at 150°C; Catalyst Loading = 1.67% of Coal; Other Parameters as in Table IV.

	COAL	$R_{TC} = 1$	$R_{TC} = 2$
LIQUEFACTION TEMPERATURE = 375°C			
X	32.9	36.0	33.4
A+P	24.4	27.6	27.2
O	7.8	6.9	5.0
G	0.8	1.6	1.2
LIQUEFACTION TEMPERATURE = 400°C			
X	62.4	66.0	60.7
A+P	40.9	50.2	46.9
O	18.8	13.4	10.7
G	2.8	2.4	3.2
LIQUEFACTION TEMPERATURE = 425°C			
X	67.0	78.1	78.1
A+P	32.7	20.2	22.8
O	28.3	15.2	13.8
G	6.1	7.3	5.0

TABLE VI

Effect of R_{TC} on Product Yields. Catalyst Loading = 1.67% of Coal + Tire. Liquefaction Temperature = 400°C. Other Parameters as in Table V.

	DECS-6	$R_{TC} = 1$	$R_{TC} = 2$
X	64.6	75.5	75.3
A+P	39.7	53.3	54.2
O	21.8	17.6	16.6
G	3.1	4.6	4.6

Figure 1. Effect of temperature, time and H_2 pressure on conversion of DECS-6 coal

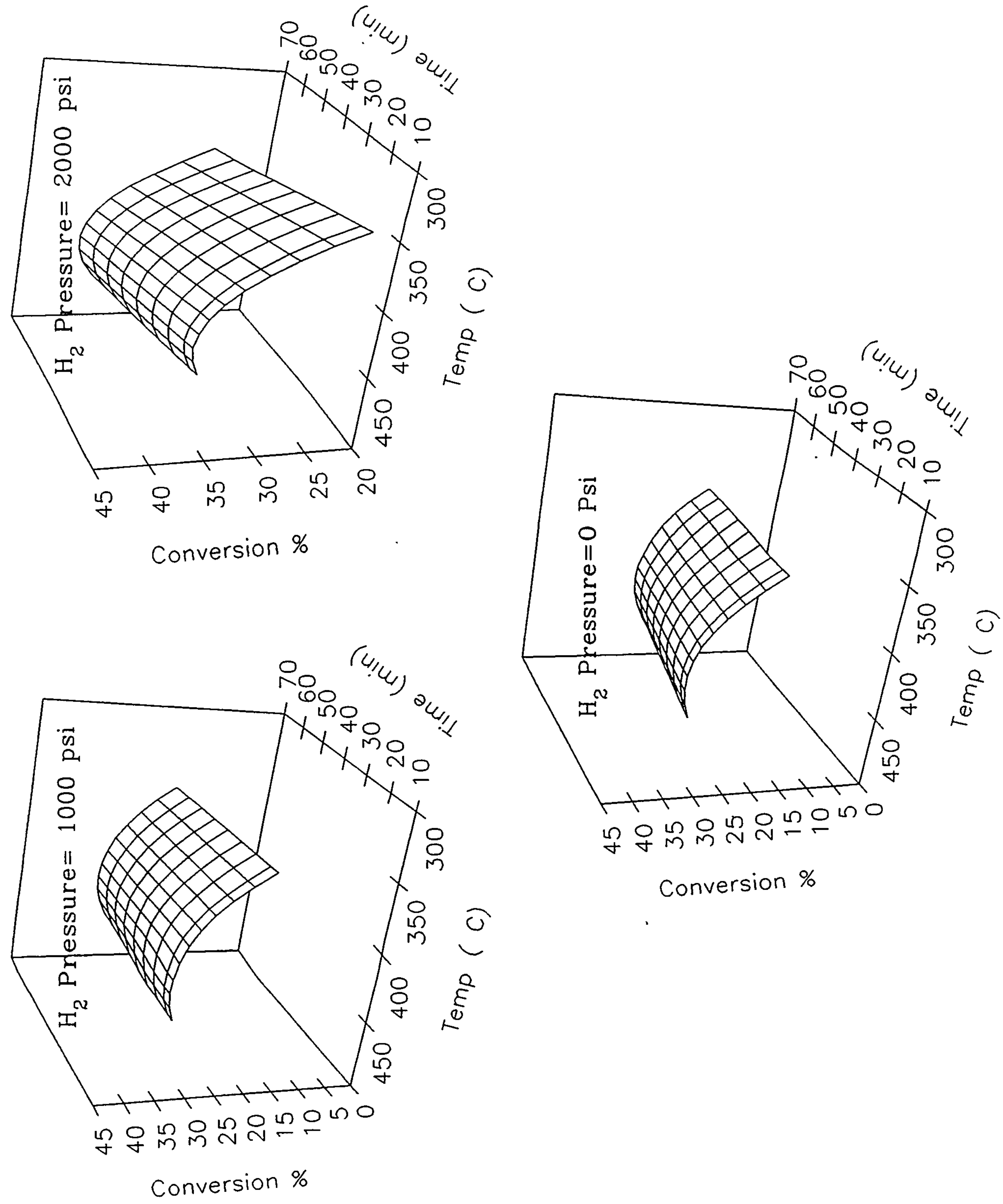


Figure 2. Conversion and product yields for DECS-6 coal at 2000 psi(hot) H_2 pressure.

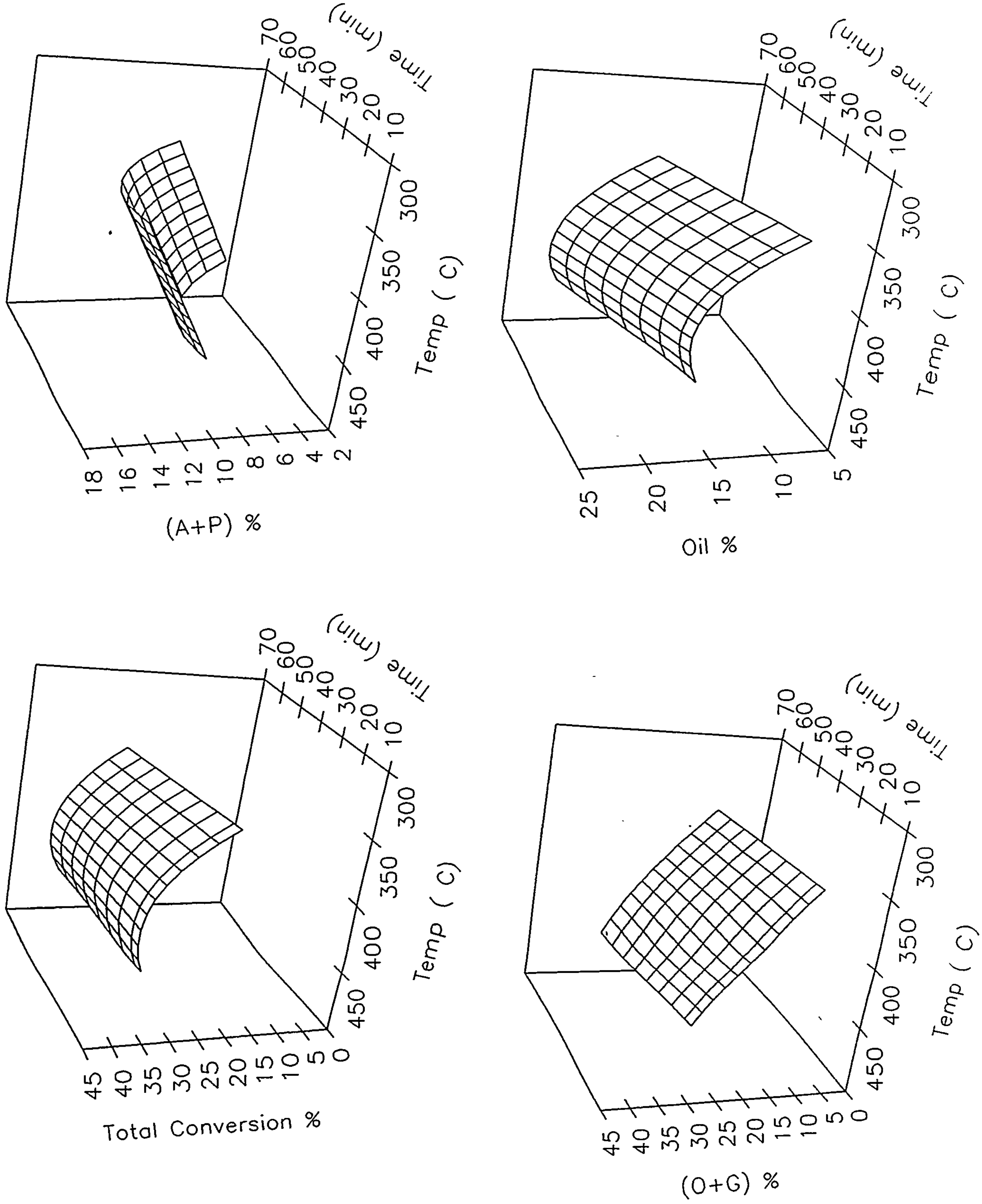


Figure 3. Conversion and product yields for Tire–2 at 2000 psi(hot) H_2pressure.

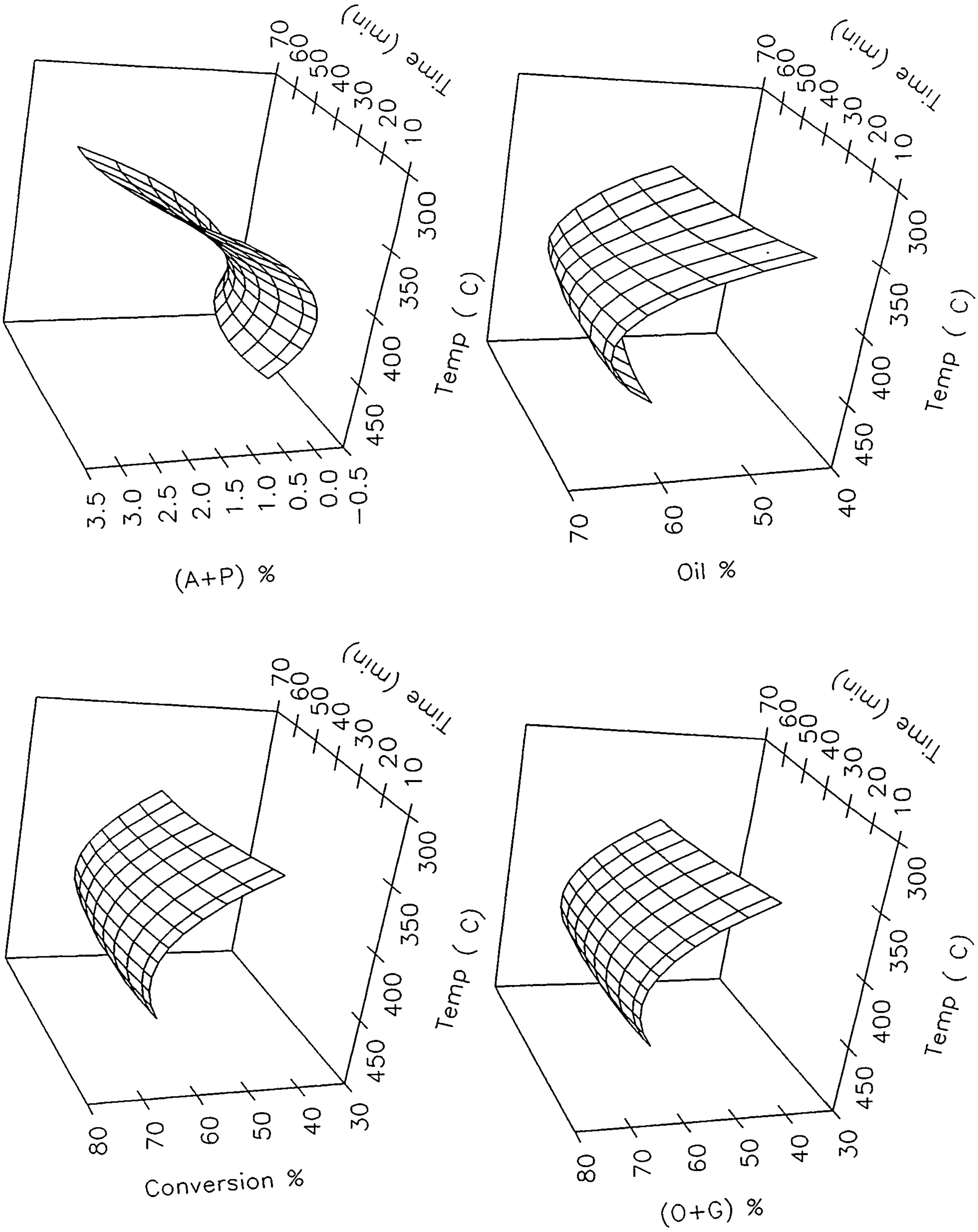
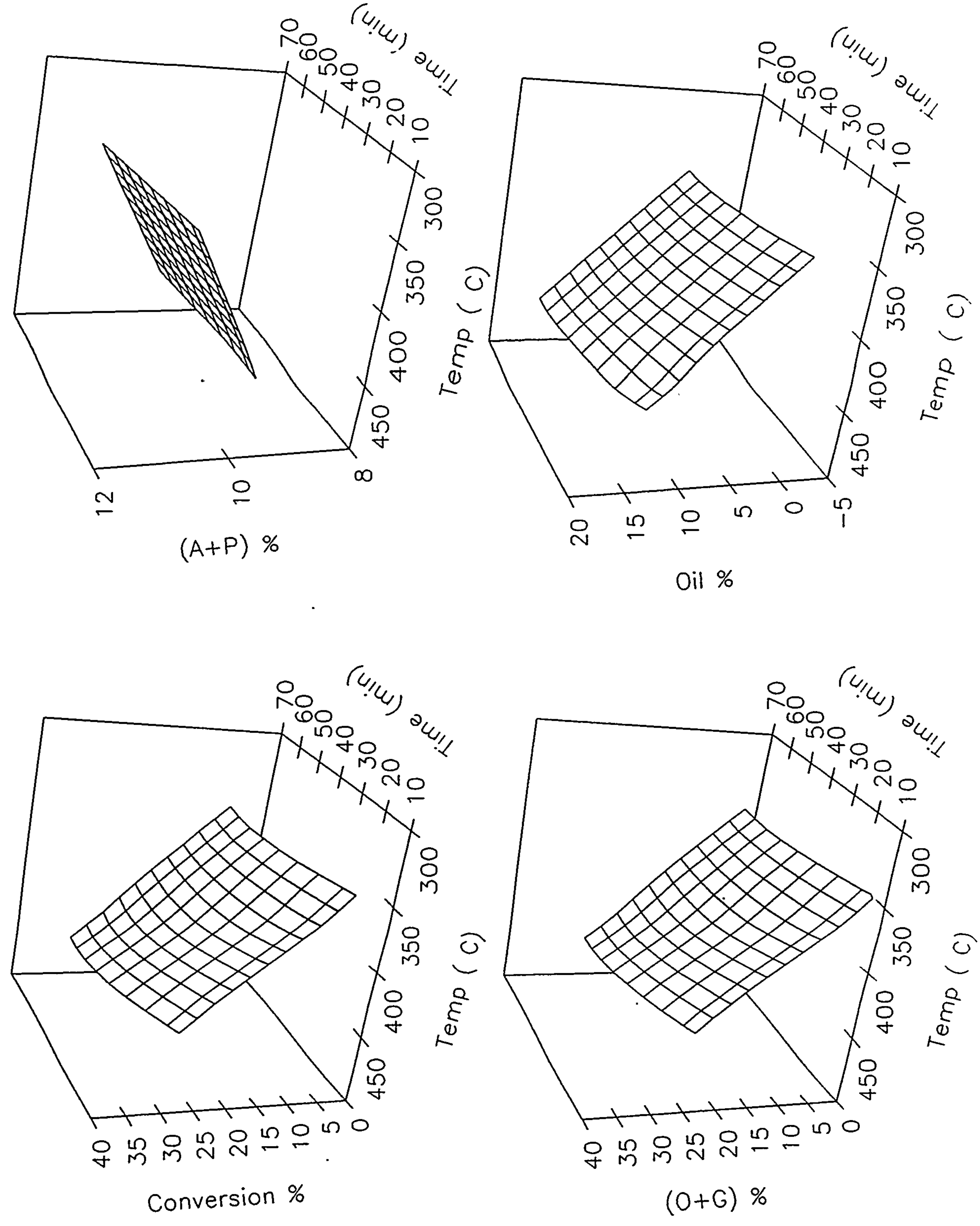


Figure 4. Conversion and product yields for DECS-26 coal at 2000 psi(hot) H_2 pressure.



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