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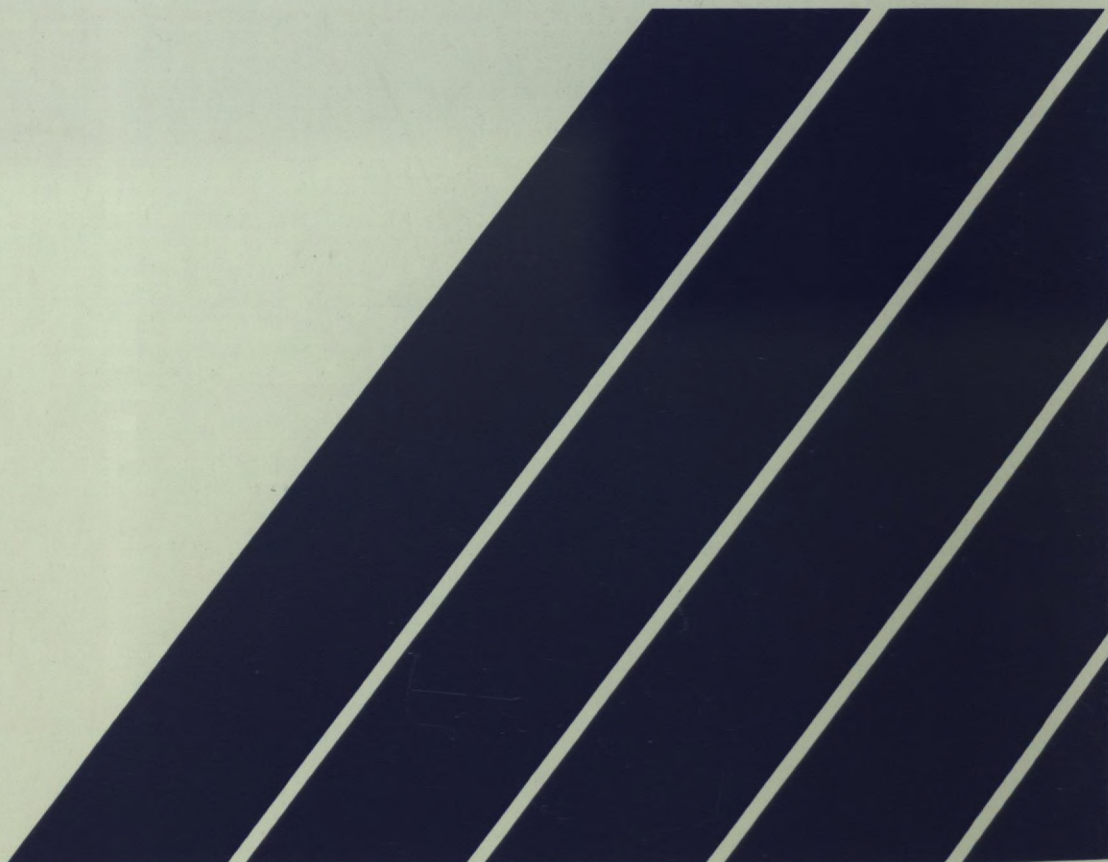
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OPTIMAL CONDITIONS FOR CANMET  
COPROCESSING OF RHEINISH COAL  
AND REFINERY VTB



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D.D.S. Liu, J.F. Kelly, M. Ikura  
Energy Research Laboratories/CANMET  
Ottawa, Ontario, Canada K1A 0G1

R.J. Torres-Ordonez  
Amoco Oil Company  
Naperville, Illinois 60566, USA

Uwe Lenz  
Rheinbraun AG  
Koln 41, German

CANMET  
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# OPTIMAL CONDITIONS FOR CANMET COPROCESSING OF RHEINISH COAL AND REFINERY VTB

D.D.S. Liu<sup>1</sup>, J.F. Kelly<sup>1</sup>, M. Ikura<sup>1</sup>,  
R.J. Torres-Ordonez<sup>2</sup> and Uwe Lenz<sup>3</sup>

## ABSTRACT

A series of coprocessing PDU experiments was conducted using 30 wt % Rheinisch brown coal and refinery vacuum tower bottoms. Runs were carried out in CANMET's hydroprocessing and process development unit (PDU) using a 10-L tubular reactor. Three key operating variables were examined: slurry space velocity, reactor temperature and superficial gas velocity. The maximum pitch (525°C+) and coal (THF insolubles) conversions were 94.3 wt % and 98.0 wt %, respectively.

Pitch, coal (THF insolubles) and asphaltene conversions were determined and properties of the products were measured. Gas holdups as a function of reactor height were measured by a narrow beam gamma-ray densitometer. Space mean holdups and effective space times, which were defined as quotients of the mean liquid holdup to the nominal weight slurry hourly space velocity, were derived.

Statistical analyses of conversions and fractional yields indicated that the responses could be characterized by temperature and effective space time. For pitch conversion, the effects of these two variables were found to be nearly independent, thus the linear model was applicable. However, the effects of the interaction of these two variables were significant for coal and asphaltene conversions.

Empirical response surfaces were generated for the presentation of experimental results. Predicted conversions and yields agree well with the experimental data. By superimposing pitch and coal conversions response surfaces, an operation domain was determined to achieve high pitch conversion and avoid significant regressive reaction.

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1. Energy Research Laboratories, CANMET, Natural Resources Canada, Ottawa, Ontario, Canada K1A 0G1
  2. Amoco Oil Company, Naperville, Illinois 60566, U.S.A.
  3. Rheinbraun AG, Koln 41, Germany

## INTRODUCTION

CANMET coprocessing is a single-stage, once-through high conversion primary upgrading process. It utilizes a slurry phase feed containing an iron-based disposable additive. The process has been developed over the past decade using both batch and continuous flow reactors (1-3). A nominal 1 kg/h bench-scale continuous flow stirred tank reactor (CSTR) and a nominal 3 kg/h bench-scale tubular reactor have been used to develop the process. A number of different coals from high-volatile bituminous to lignites combined with various vacuum tower bottoms (VTB) have been evaluated as coprocessing feedstocks (2,3).

The CANMET Coprocessing Consortium was established in 1989. Research valued at approximately \$1 M annum was carried out for three years. The work was directed by a management steering committee comprising Amoco, Rheinbraun AG, Alberta Oil Sands Technology Research Authority (AOSTRA) and CANMET. Rheinisch brown coal from Germany and a refinery VTB from USA were combined to examine the feed flexibility of the process. The slurry was tested in a bench-scale 1 kg/h CSTR unit and in the 350 kg/d process development unit (PDU).

Eight PDU runs were done using slurry feed containing 30 wt % (maf basis), Rheinisch brown coal and the VTB. These runs were designed to examine the effects of slurry space velocity, reactor temperatures and recycle gas rate. A wide range of operating parameters were used. This paper describes some of the results and the application of statistical methods to analyze the experimental results. This approach enabled us to determine optimal process conditions for achieving high pitch conversion and avoiding significant regressive reaction.

## EXPERIMENTAL AND RESULTS

Experiments were carried out in CANMET's process development unit (Fig. 1). The reactor is a 10-L slurry bubble column (5.08 cm ID and 493 cm long). Internal temperatures along the reactor were monitored by seven thermocouples and were controlled by eight electrical heaters. The reactor was also equipped with four hydrogen quenching systems to



control reaction parametric sensitivity. Control and data acquisition mechanisms for the PDU were computerized.

Seven sampling ports were used to characterize the properties of the reactor contents. A narrow-beam gamma-ray scanner (4) was used to measure gas holdups along the reactor axis at various operating conditions.

Predetermined amounts of coal, VTB and CANMET additive were mixed in a feed tank. The slurry was pumped into the system and combined with the recycle gas. The mixture passed through the slurry preheater then was fed to the reactor bottom. The reactor was operated in an upflow concurrent slurry bubble column mode. The reactor effluent passed through a small diameter cross-over line into a hot separator which was maintained at an elevated temperature. The exiting vapour was cooled and condensed in a cold separator. The discharged hot and cold liquid streams resulted in heavy end and light end products. The uncondensed gases passed through water and oil scrubbers in series to control the hydrogen purity. A hydrogen makeup stream counteracted the pressure loss in the system caused by the off-gas discharges. The inlet and discharge streams were monitored continuously and their properties were measured.

Run conditions are given in Table 1. The experiments were designed to examine a wide range of temperatures, feed rates and gas rates. Also only pitch conversions above 55 wt % were considered. Properties of VTB and coal are given in Tables 2 and 3.

Table 4 gives conversions of pitch (525°C+), coal (THF insolubles) and asphaltenes (TI solubles and pentane insolubles).

## STATISTICAL ANALYSIS

The effects of temperature, feed rate and gas rate on conversions, product yields and operability were examined. A full 3-parameter 2 factorial ( $2^3$  factorial) design requires eight runs. The design recommends conditions located at the apexes of the condition cube (5). The experimental conditions for the eight PDU runs were selected based on the interests of participants in the consortium. They deviate greatly from the recommended design conditions. Thus, an attempt to analyze the results by a  $2^3$  factorial design resulted in large uncertainties.

The gas rate (which is uniquely correlated with liquid holdup) and the nominal weight hourly space velocity (WHSV) were transformed into an effective space time according to the following formula:

$$\text{Effective space time } (\tau) = (\text{Liquid holdup}) / (\text{WHSV})$$

After the parameter transformation, the conditions for the experiment can be presented by a 2-parameter space with temperature and effective space velocity as coordinates (Fig. 2) (Table 1). The responses including conversions and fractional yields were then analyzed by a statistical program DESIGN-EXPERT (6). Linear and quadratic models were tested and the better was adopted.

Although only one experiment in the long effective space time region was carried out, the data were sufficient for the "decomposition" to estimate the values at the apex conditions for carrying out the  $2^2$ -factorial analyses in the temperature-space time space (Fig. 2).

When either a linear or quadratic model was chosen for a given parameter, the data were fitted by a standard regression method to generate the response surfaces and interaction plot, both of which were found in some cases to be only slightly different from those computed by DESIGN-EXPERT.

Figures 3 and 4 show the response surface and an iso-response projection plot for pitch conversions. The interaction plot is given in Fig. 5. The high and low space time lines are nearly parallel, indicating that the effects the interaction between temperature and space time is insignificant.

The quadratic model had a better fit for coal and asphaltenes conversions. The response surface and iso-response projection diagram for the coal conversion are shown in Fig. 6 and 7. Figure 8 shows the interaction plot for coal conversion. Although the effect of temperature was small (all coal conversions > 85 wt %), the effect of the interaction between temperature and space time was significant. The region near the  $T_+, \tau_+$  corner was particularly important, because the process was normally targeted to obtain a high pitch conversion (Fig. 7). However, the coal conversion decreased when the operation was closer to this apex, indicating a tendency of increasing retrogressive reaction. Since the simple quadratic model is designed in such a way that a symmetrical response surface (in this case it is saddle shaped) would be produced, the predictions for the  $T, \tau_+$  region, which are not the conditions of interest, bear no significance.

The response surface and the iso-response projection diagram for the asphaltene conversions are shown in Fig. 9 and 10. The interaction between temperature and space time was important as indicated by the rising ridge shape of the response surface (Fig. 11) and the non-parallel interaction plot (Fig. 11). At a low effective space time, the temperature had little effect on asphaltene conversion (horizontal line in Fig. 11). However, at a high effective space time, the temperature had a strong positive effect.

## DISCUSSION AND CONCLUSIONS

Experimental results of PDU runs using Rheinisch brown coal and a refinery VTB are presented. The conversions of pitch, coal and asphaltenes for coprocessing can be statistically modelled by temperature and effective space time.

The effective space time,  $\tau$ , is a good parameter whose impact on the process represents the combined effects of slurry throughput and space mean voidage. From the statistical analysis, many important features of the process can be characterized. For instance, if the response was characterized by a linear model, e.g., pitch conversion or naphtha yield, the effects of temperature or apparent space time are independent, whereas when a quadratic or higher order model is applicable the effects of interaction between parameters must be considered.

The response surfaces are also useful for optimizing operating conditions which is highly desired in industry. For instance, if an operation aims to achieve high pitch conversion and avoid significant regressive reaction at a coal conversion of  $\geq 94$  wt %, the domain for operation can be determined by superimposing the pitch and coal conversion response surfaces. Figure 12 shows the operable region (unshaded area) for a pitch conversion of  $\geq 90$  wt %. Note that run 5 is enclosed in this region. Accordingly, the effective space time is controlled by the throughput, WHSV and the gas voidage. The latter is a function of gas rate, temperature and reactor geometry. It can be monitored online in either pilot scale or commercial reactors. Since the gas holdup in this domain does not vary significantly, the apex at the low space would be the best condition because it operates at the maximum slurry throughput.

The effects of dispersion and product vaporization were grouped into the effective

space time. Without detailed information on these effects, it is difficult to apply a kinetic model associated with an axial dispersion model or plug flow model. Our work has shown that the empirical statistical models can offer an alternative approach. In particular, it has proven to be capable of modelling all of the major responses for a very wide range of operating conditions.

### ACKNOWLEDGEMENT

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### REFERENCES

1. Kelly, J.F, Fouda, S.A., Rahimi, P.M. and Ikura, M., REPRINTS, CANMET Coal Conversion Contractors' Review Meeting (1984).
2. Fouda, S.A. and Kelly, J.F., REPRINT, the USDOE Direct Liquefaction Contractors' Review Meeting, Pittsburgh, PA (1985).
3. Fouda, S.A. and Kelly, J.F., Proceedings of the 1987 Interactional Conference on Coal Science, Elsevier, Amsterdam, 899 (1987).
4. Liu, D.D.S. and Patmore, D.J., Int. J. Radiat. Appl. Instrum. Part. A, Appl. Radiat. Isot., 41(10/11), 1003-1012 (1990).
5. Box, G.E.P., Hunter, W.G. and Hunter, J.S. "Statistics for experimenters, an introduction to design, data analysis, and model building", NY, John Wiley (1978).
6. DESIGN-EXPERT, STAT-EASE, Inc. (1989).



Table 1 - Run conditions

Run	1	2	3	4	5	6	7	8
Temperature (°C)	440	440	450	450	450	457	457	457
Relative temperature*	-1	-1	0.176	0.176	0.176	+1	+1	+1
Hydrogen purity (%)	84.5	85.9	83.1	83.9	85.8	85.5	84.9	85.9
Duration (h)	22	24	24	20	24	24	24	25
Effective space time (L-h/kg)	0.776	0.524	0.908	0.617	1.773	0.869	0.651	0.561
Relative effective space time*	-0.596	-1	-0.385	-0.854	+1	-0.448	-0.797	-0.941

\* Linearly scaled values. The limits -1 and +1 correspond to minimum and maximum values, respectively.

Table 2 - Properties of the refinery VTB as received

Pitch content	wt %	86.0
Density	g/mL	1.024
Gravity	°API	6.7
Ash	wt %	0.05
Carbon	wt %	85.0
Hydrogen	wt %	10.3
Nitrogen	wt %	0.47
Oxygen	wt %	—
Sulphur	wt %	4.22
Vanadium	ppm by AA	217
Nickel	ppm by AA	61
Iron	ppm by AA	9
Pentane insolubles	wt %	19.2
Toluene insolubles	wt %	0.24
THF insolubles	wt %	0.0
Asphaltenes	wt %	18.96
Preasphaltenes	wt %	0.24
MCR	wt %	20.7
Aromaticity	wt %	37
IBP (D-1160)	°C	196
Viscosity		
at 100°C	cSt	1030
	cP	1054
at 120°C	cSt	457
	cP	468
at 135°C	cSt	209
	cP	214

Table 3 - Properties of Rheinisch brown coal (average of two samples: large and small sizes)

	As received	Dry at 105°C	maf
Moisture	12.9 ± 0.1		
Ash	4.46 ± 0.08	5.12 ± 0.09	
Volatile material			51.9 ± 0.1
Carbon	57.1 ± 0.2	65.5 ± 0.2	69.0 ± 0.3
Hydrogen	4.10 ± 0.01	4.71 ± 0.01	4.96 ± 0.01
Nitrogen	0.70 ± 0.01	0.80 ± 0.01	0.84 ± 0.02
Sulphur: Total*	0.14 ± 0.04	0.24 ± 0.06	0.25 ± 0.06
Oxygen (by diff)	20.6 ± 0.2	23.7 ± 0.3	24.9 ± 0.3

\* Mainly organic sulphur; sulphate and pyritic sulphur are non-measurable.

#### Calorific analysis

Cal/g	5330 ± 11	6119 ± 12	6449 ± 7
BTU/lb	9594 ± 20	11014 ± 21	11608 ± 11

#### Ash analysis (wt % in ash)

SiO <sub>2</sub>	4.65 ± 0.07
Al <sub>2</sub> O <sub>3</sub>	4.77 ± 0.22
Fe <sub>2</sub> O <sub>3</sub>	17.51 ± 0.92
TiO <sub>2</sub>	0.25 ± 0.03
P <sub>2</sub> O <sub>5</sub>	0.33 ± 0.08
CaO	35.5 ± 0.9
MgO	14.7 ± 0.6
SO <sub>3</sub>	17.5 ± 0.5
Na <sub>2</sub> O	0.64 ± 0.24
K <sub>2</sub> O	0.27 ± 0.05
BaO	0.35 ± 0.01
SrO	0.25 ± 0.01
V <sub>2</sub> O <sub>5</sub>	0.0
NiO	0.01 ± 0.01
LOF	3.12 ± 0.89

Table 4 - Conversions and yields

Run	1	2	3	4	5	6	7	8
Pitch conversion (wt %)	62.9	57.0	73.1	68.6	94.3	81.0	77.7	71.2
Coal (THFI)* conversion (wt %)	93.1	85.1	94.1	90.2	98.0	92.7	93.6	92.1
Asphaltene conversion (wt %) .	43.2	43.3	49.0	44.2	72.2	54.7	51.6	40.7

\* THF insolubles

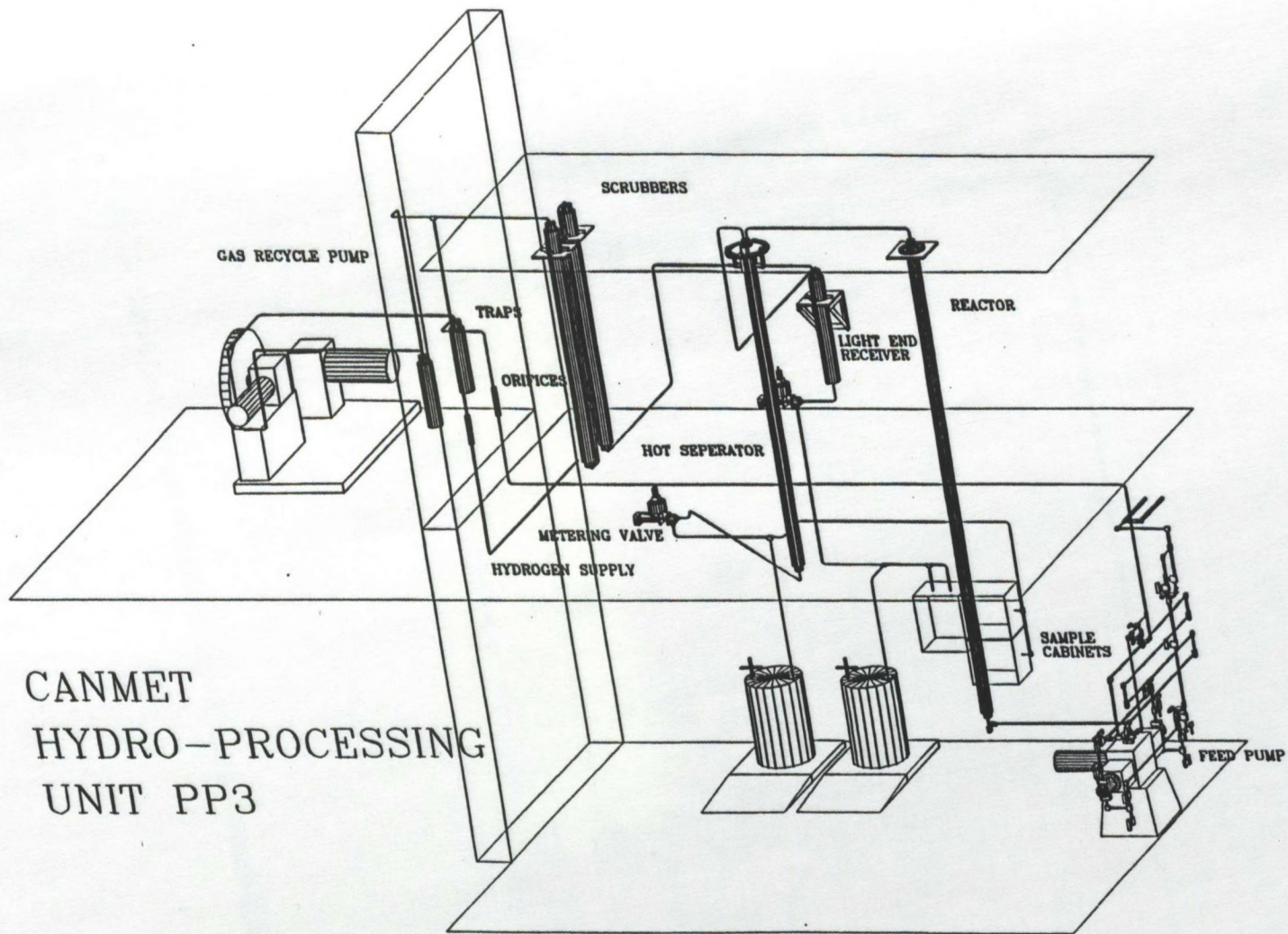


Fig. 1 - Schematic of CANMET process development unit



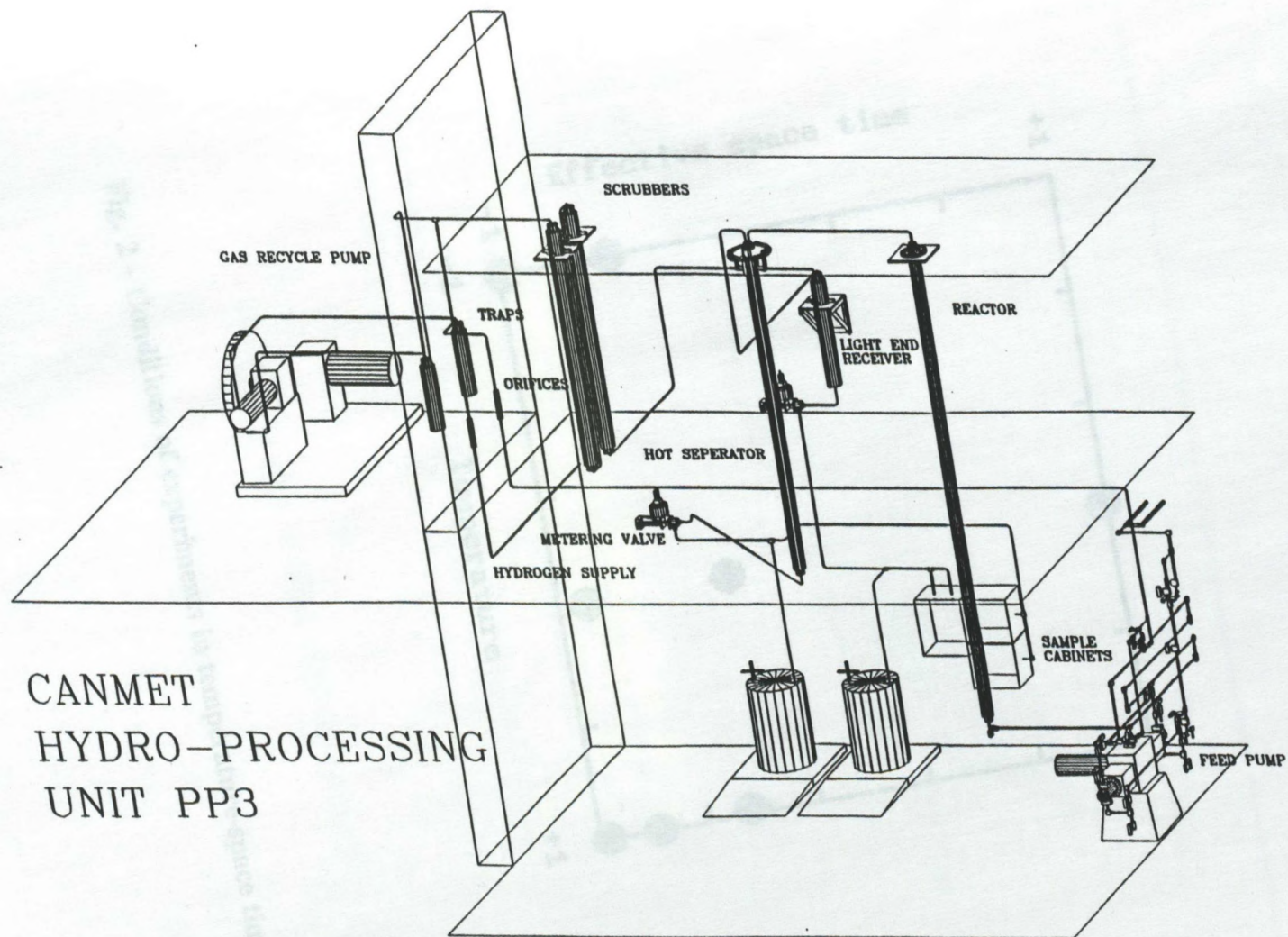


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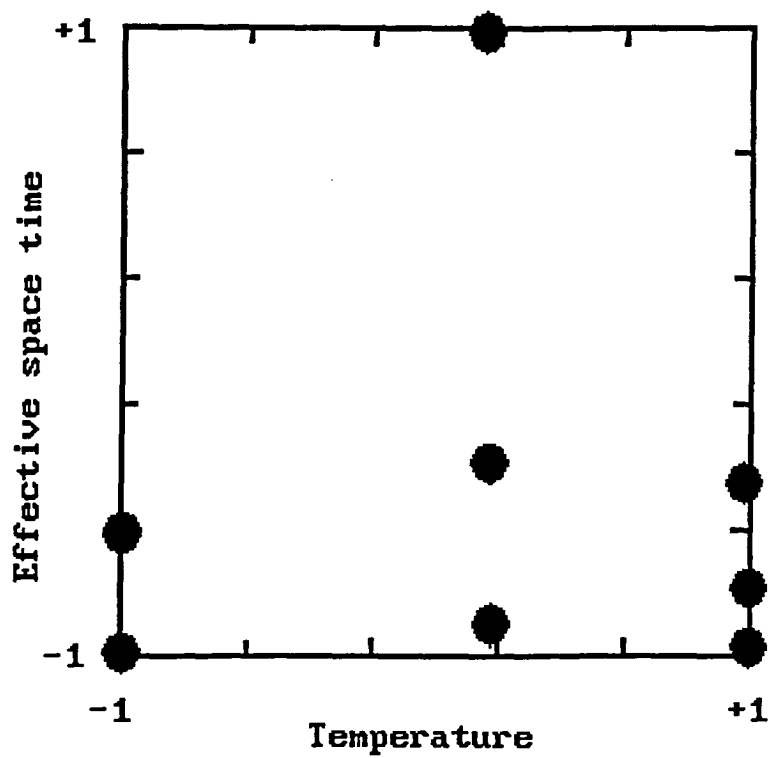
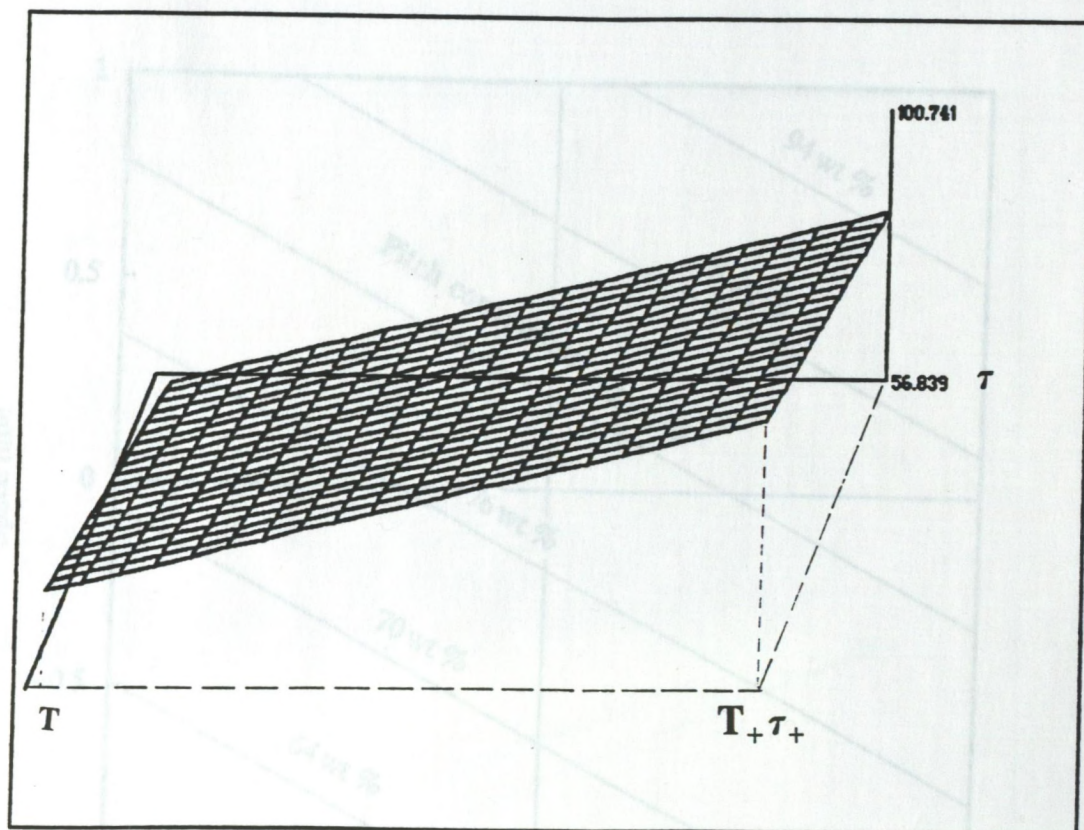


Fig. 2 - Conditions of experiments in temperature-space time space



**Fig. 3 - Response surface of pitch conversion**

**Fig. 4 - Iso response plot for pitch conversion**

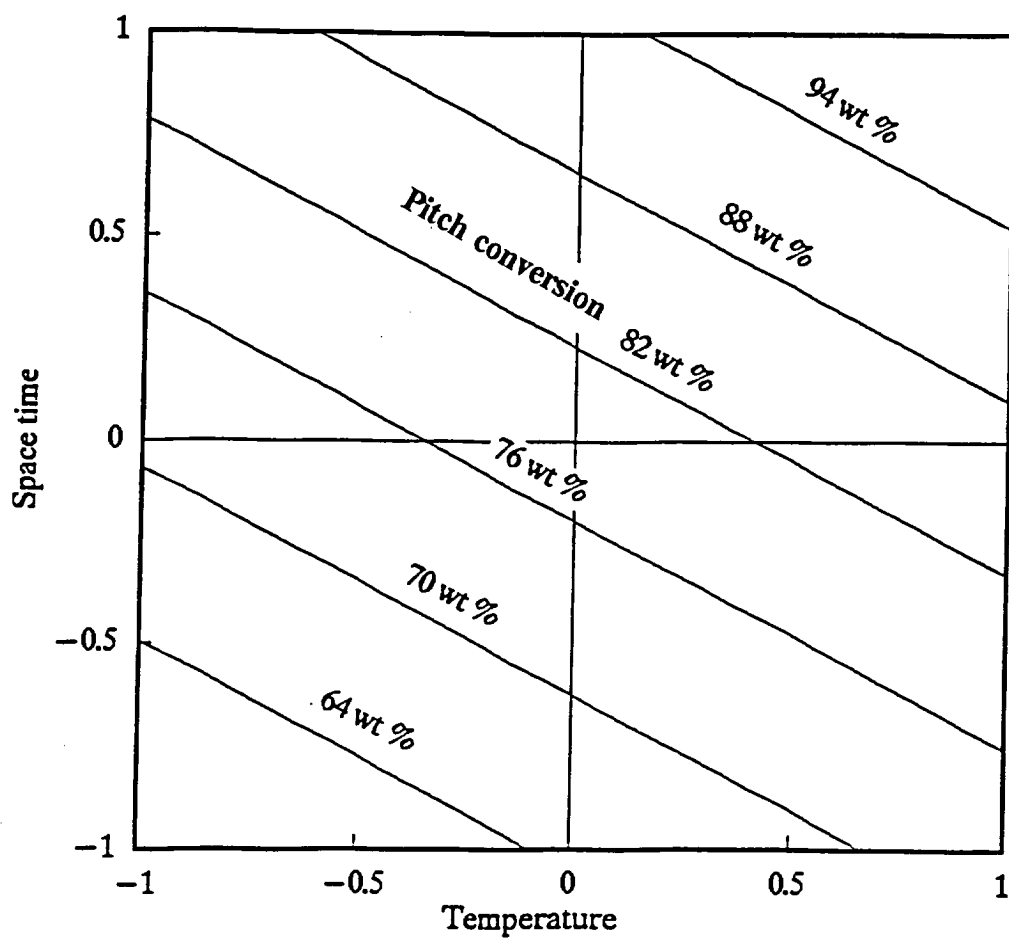


Fig. 4 - Iso-response plot for pitch conversion

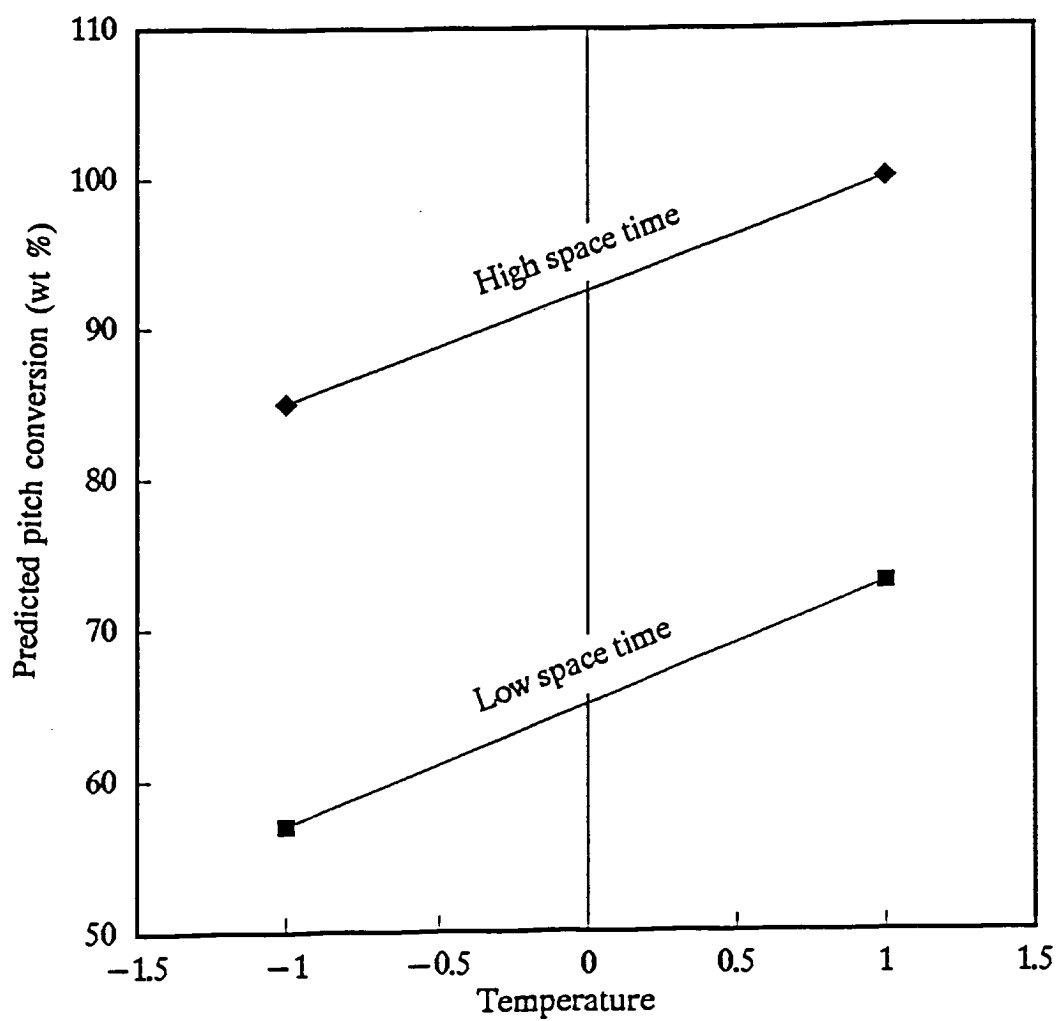
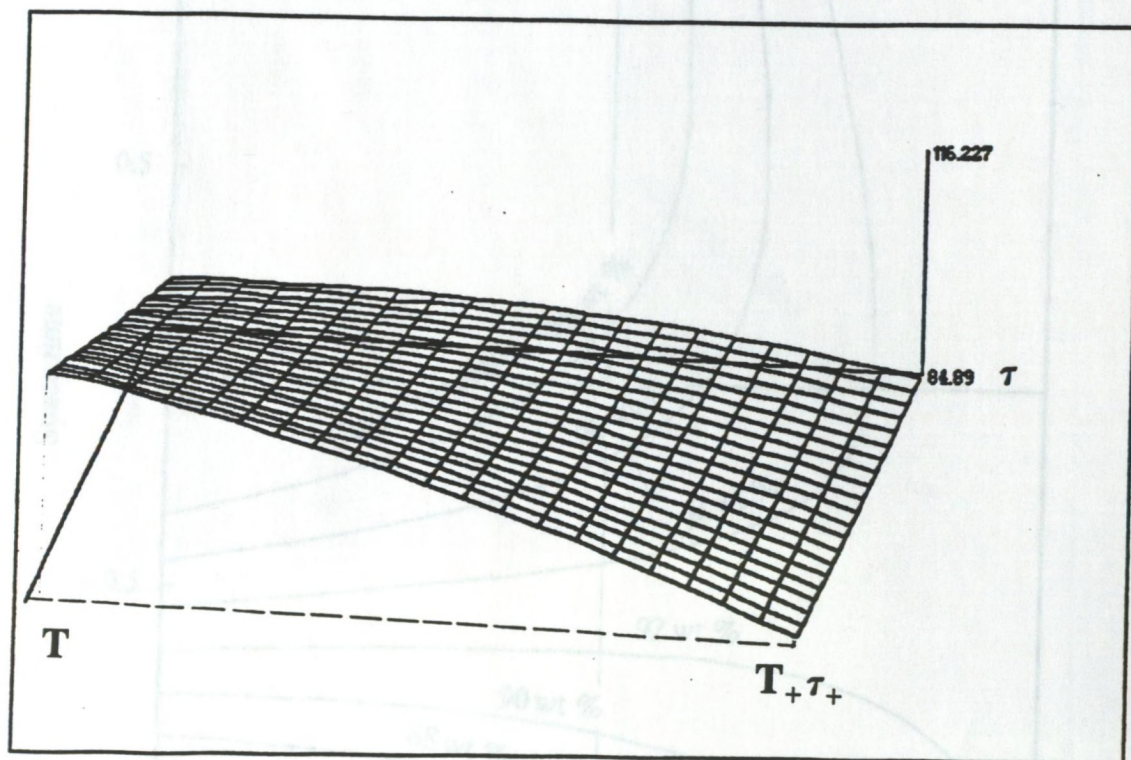


Fig. 5 - Parameter interaction plot for the response of pitch conversion





**Fig. 6 - Response surface of coal conversion**

*Fig. 7 - Iso-response plot for coal conversion*

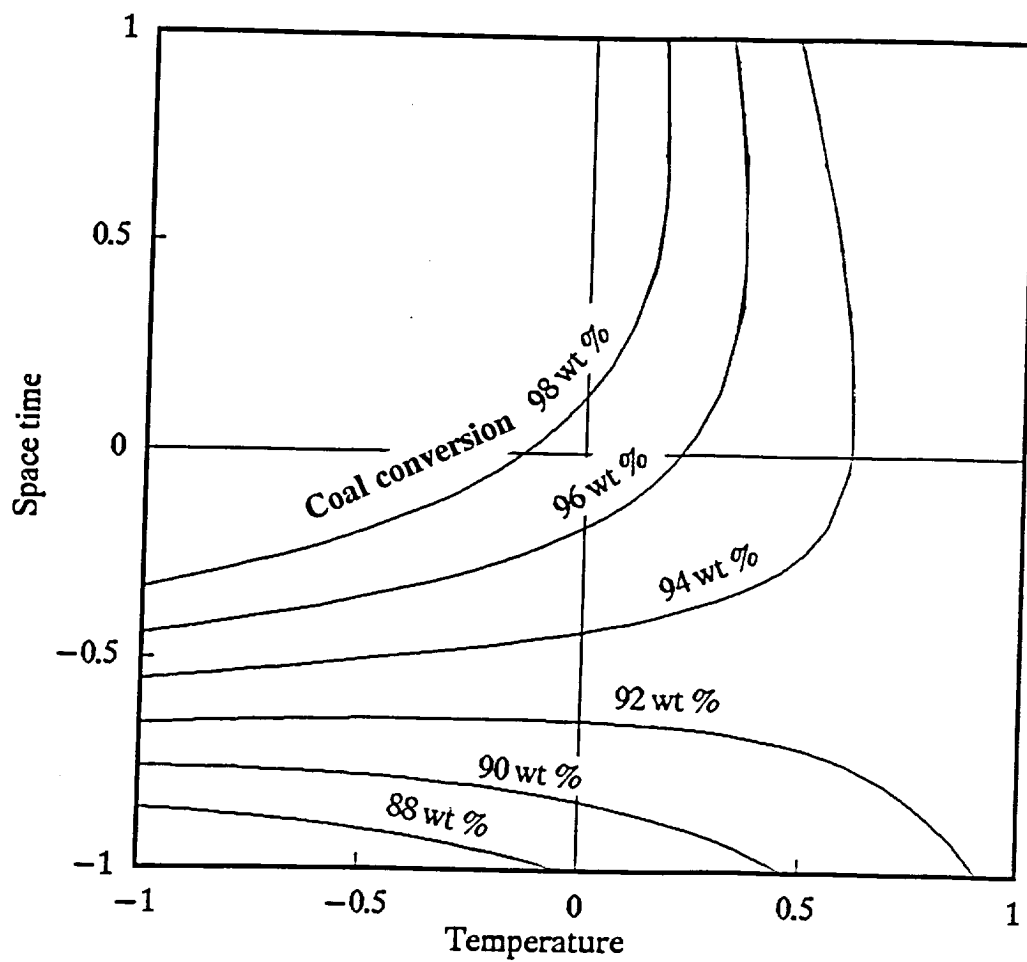


Fig. 7 - Iso-response plot for coal conversion



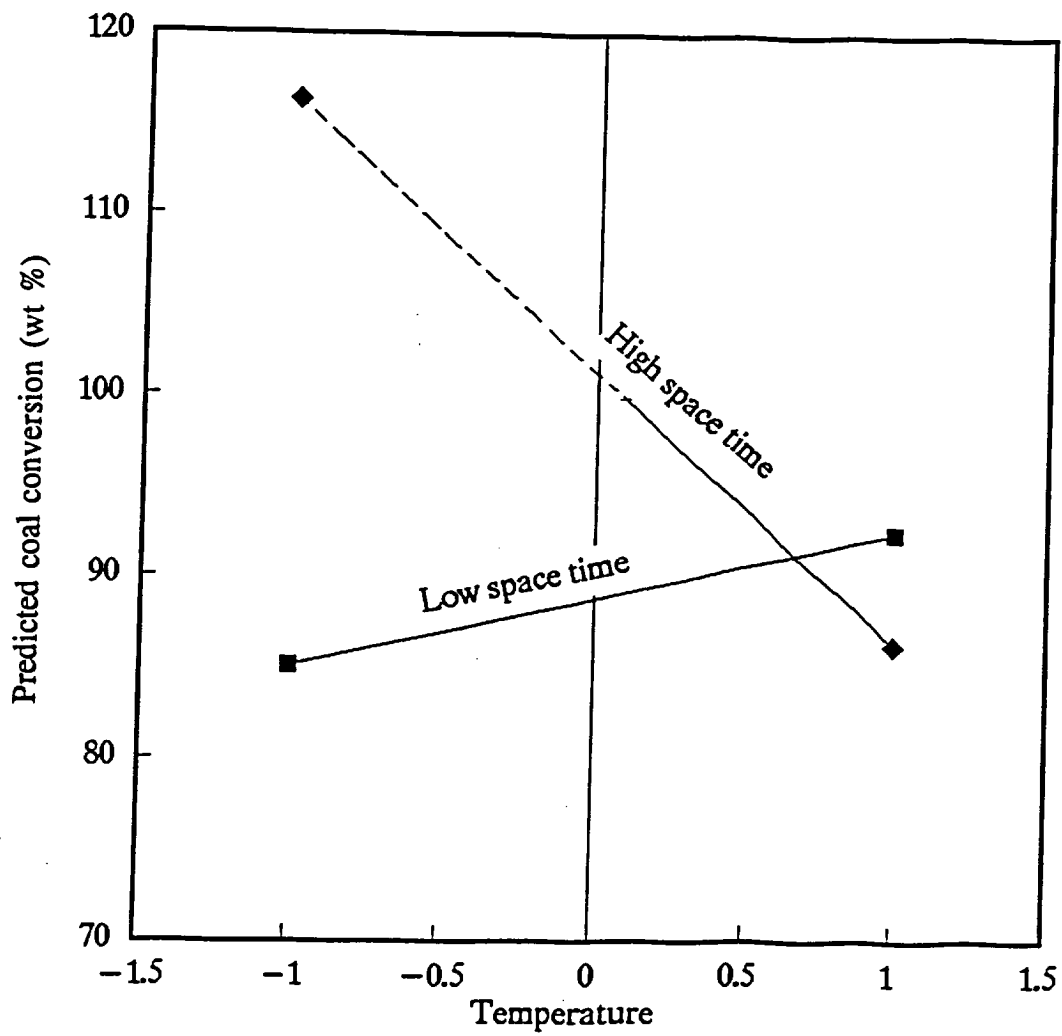
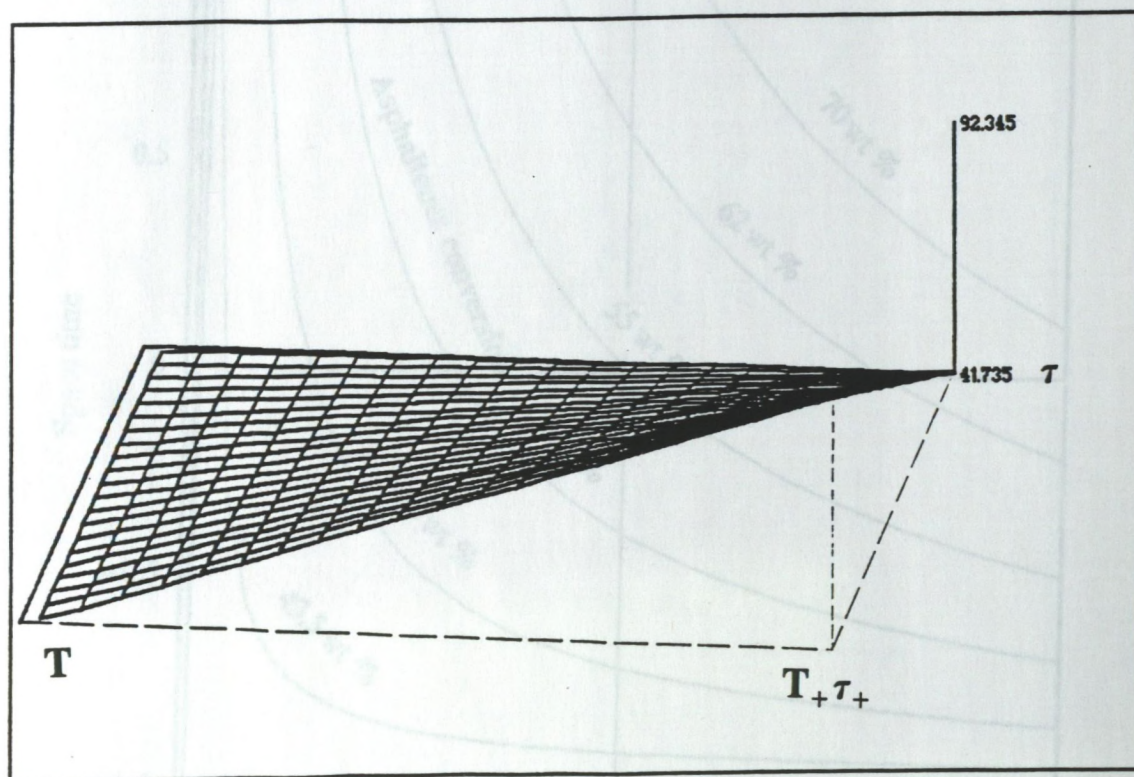


Fig. 8 - Parameter interaction plot for the response of coal conversion



**Fig. 9 - Response surface of asphaltene conversion**

**Fig. 10 - Iso-response plot for asphaltene conversion**

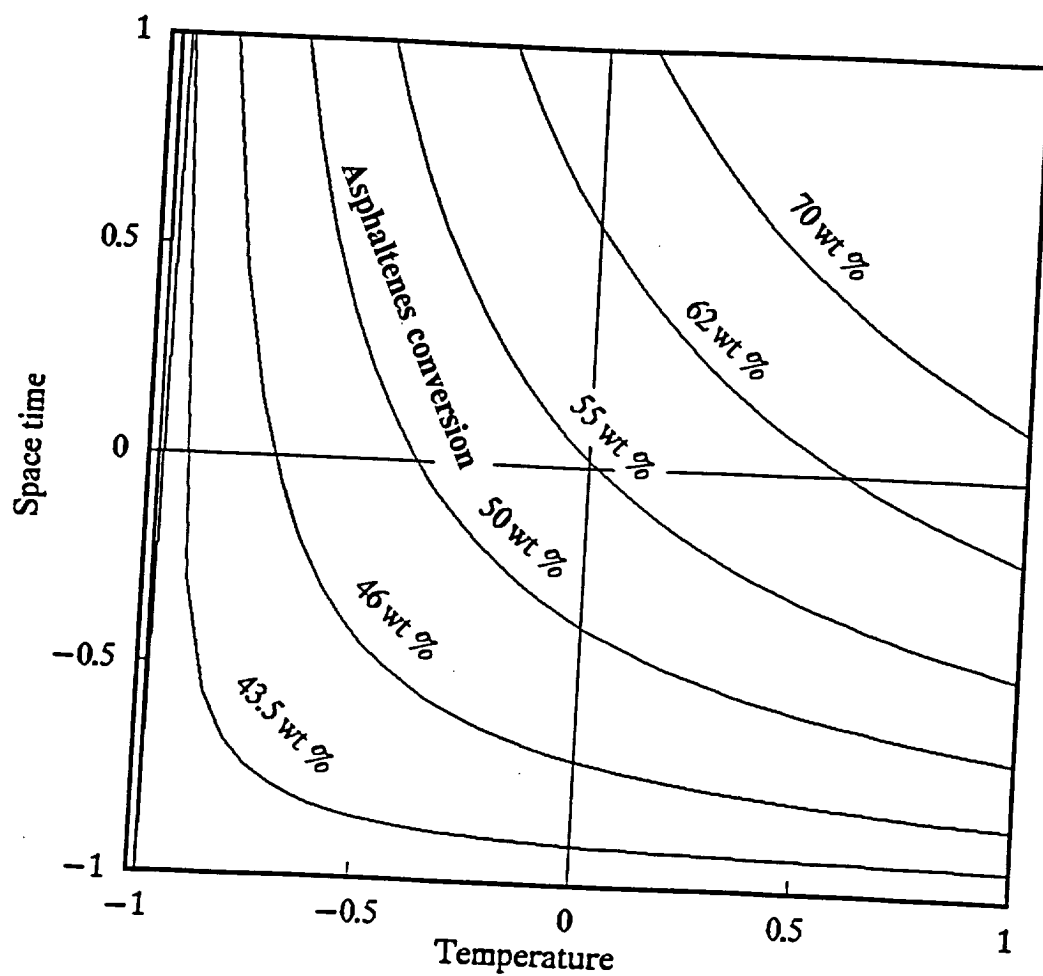


Fig. 10 - Iso-response plot for asphaltene conversion

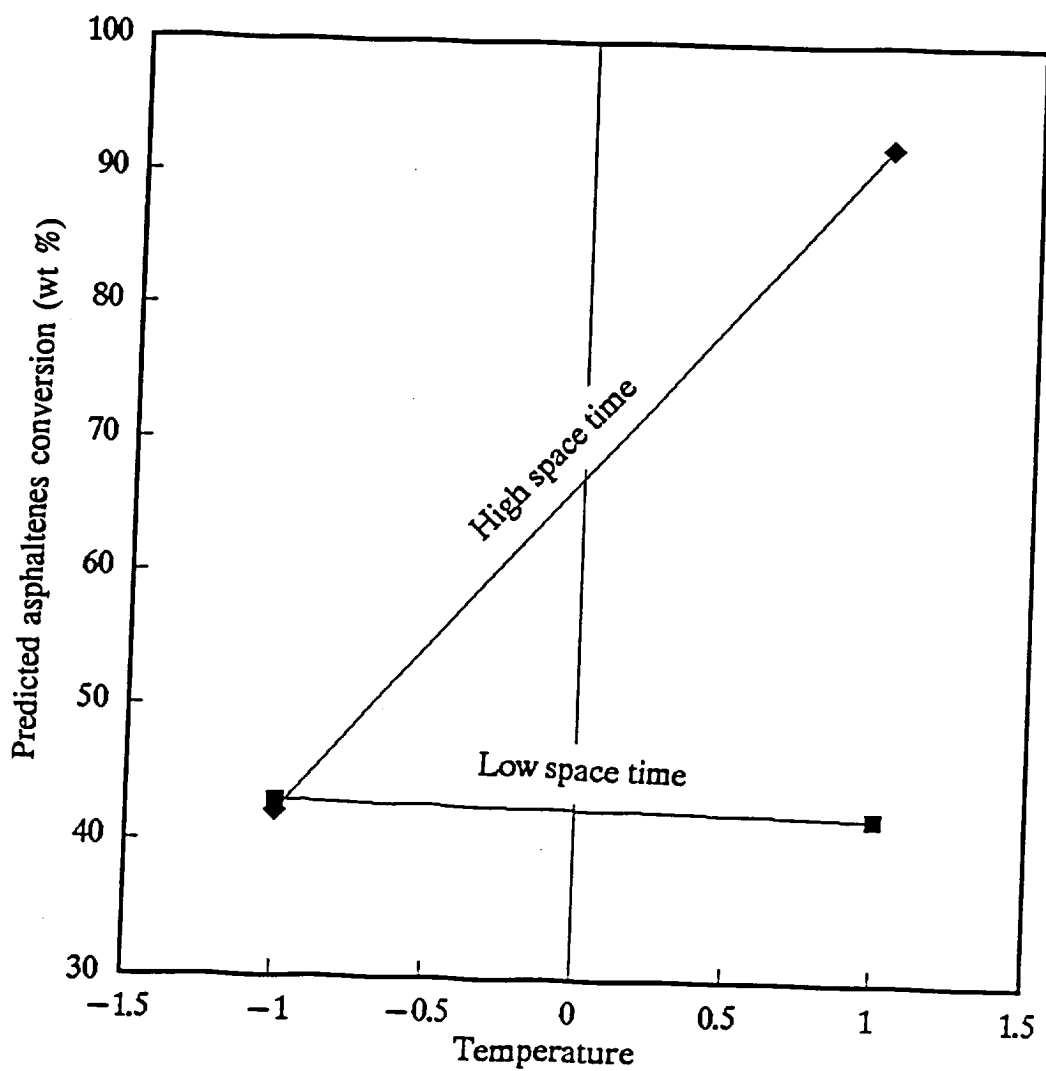
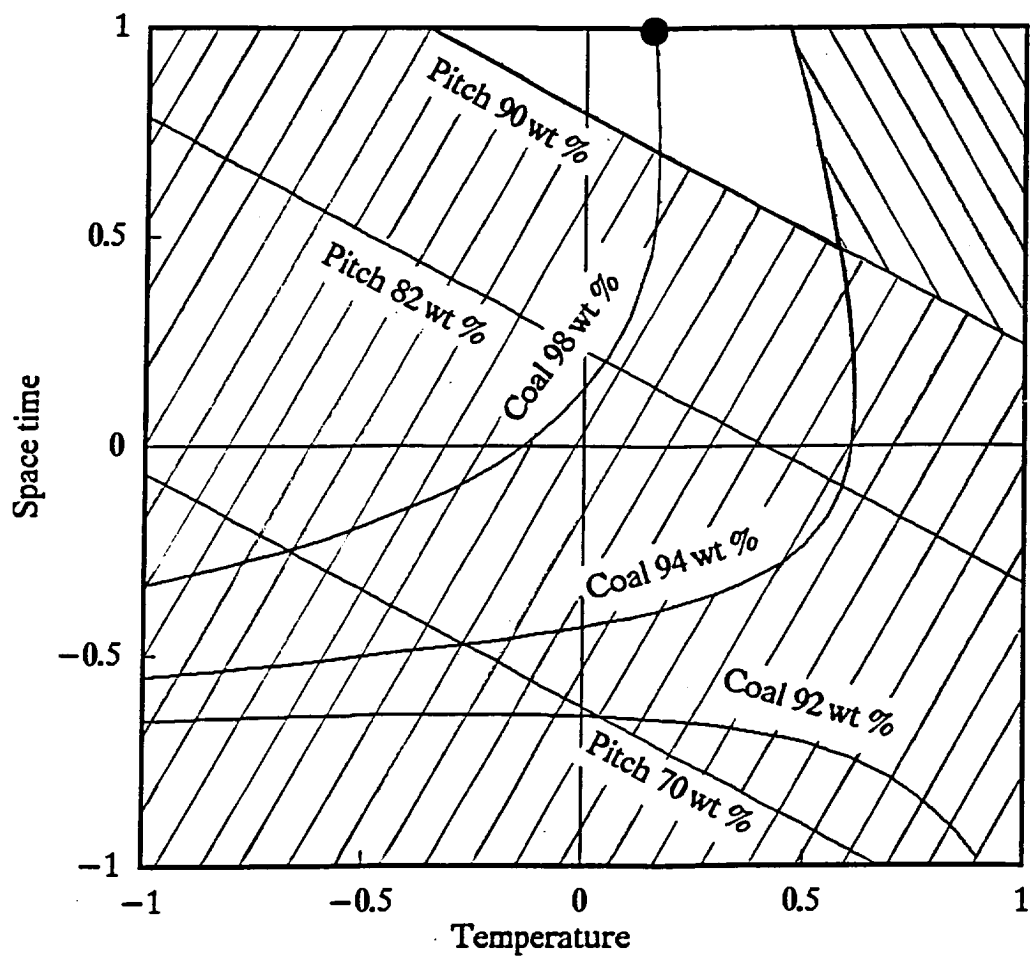


Fig. 11 - Parameter interaction plot for the response of asphaltene conversion



**Fig. 12 - Modelled operable region for achieving  $\geq 90$  wt % pitch conversion with coal conversion  $\geq 94$  wt %**

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☐ Chemical Engineer  
Other \_\_\_\_\_

Dirkson D.S. Liu

J.F. Kelly, M. Ikura

R.J. Torres-Ordonez

Uwe Lane

CANMET/ERL, NRCan  
c/o 555 Booth St., Ottawa, ON, Canada  
Amoco Research, Chicago, Illinois  
Rheinbraun AG, Kohn, Germany

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