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# SOLVOLYSIS LIQUEFACTION OF KANSAS COALS

by

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TABLE OF CONTENTS


| | | Page |
|---|---|---|
| CHAPTER I. | INTRODUCTION | I-1 |
| CHAPTER II. | DONOR SOLVENT COAL LIQUEFACTION | |
| | Literature Review | II-1 |
| | liquefaction fundamentals | II-2 |
| | donor solvent liquefaction processes | II-5 |
| | Concluding Remarks | II-10 |
| | References | II-11 |
| CHAPTER III. | SOLVOLYSIS LIQUEFACTION OF A KANSAS COAL: An Experimental Study | |
| | Introduction | III-1 |
| | Experimental | III-3 |
| | Results and Discussion | III-7 |
| | effect of reaction time | III-7 |
| | effect of reaction temperature | III-8 |
| | effect of solvent-to-coal weight ratio | III-9 |
| | stream analysis | III-11 |
| | separation solvent effect | III-13 |
| | Conclusions | III-14 |
| | References | III-15 |
| CHAPTER IV. | SOLVOLYSIS LIQUEFACTION OF FOUR KANSAS COALS: The Effect of Ash Content | |
| | Introduction | IV-1 |
| | Experimental | IV-3 |

Page

Results and Discussion . . . . . IV-6

effect of ash content on percent reduction of DAF solids . . . . . IV-6

effect of ash content on product distribution . IV-8

Conclusions. . . . . IV-10

References . . . . . IV-11

CHAPTER V. RECOMMENDATIONS FOR FUTURE WORK

Concluding Remarks . . . . . V-1

Appendix 1. Experimental Results: Solvolysis Liquefaction of a Kansas Coal . . . . . V-3

Appendix 2. Experimental Results: Solvolysis Liquefaction of Four Kansas Coals . . . V-54

# CHAPTER I

# INTRODUCTION

The aims of this work were: first, to compare the solvolysis liquefaction of various Kansas coals with reported conversions of other coals in the literature; second, to study the effects of reaction time, temperature, and solvent-to-coal weight ratio on the liquefaction of a specific Kansas coal via the Kyushu-Koshi solvolysis process; third, to study the effect of ash content in the liquefaction process using four Kansas coals; and finally, to make recommendations regarding future research.

Chapter II contains a review of the current Kansas coal situation. The potential benefits of a coal liquefaction scheme are discussed. Liquefaction fundamentals, as they are presently understood, are discussed along with recent results and implications published in the literature. A review of the Solvent Refined Coal, Exxon Donor Solvent, and Kyushu-Koshi solvolysis processes is given as a comparison of operating conditions and product compositions.

The experimental portion of this work is contained in Chapters III and IV. Chapter III presents the effects of reaction time, temperature, and solvent-to-coal weight ratio on the liquefaction of Baxter coal using the Kyushu-Koshi solvolysis process. In Chapter IV, the effect of ash content on liquefaction conversion was studied using four Kansas coals.

Chapter V presents overall conclusions and suggestions for further research relating to the work presented here.

# CHAPTER II

# DONOR SOLVENT COAL LIQUEFACTION

# LITERATURE REVIEW

This section contains a review of the current Kansas coal situation, coal liquefaction fundamentals, and a brief description of three donor solvent coal liquefaction systems.

The projected decline in available crude oil supplies presents a problem to a nation whose economy is based on massive consumption of petroleum in the form of consumer goods and energy sources. Although petroleum reserves have been drastically reduced, an abundant energy and hydrocarbon resource remains available in the form of coal deposits throughout the United States.

In 1970, Kansas ranked 8th among states west of the Mississippi River in coal production. The seven types of coal currently mined in Kansas are primarily high volatile bituminous A grade coal. These are presently strip mined in Crawford, Cherokee, and Linn Counties, in the southeastern portion of the state. From an original reserve of 500 million tons (450 million metric tons), 226 million tons (210 million MT) remain available for recovery. Kansas coals are relatively high in sulfur and ash content, 2.6 - 5.0% and 5 - 34%, respectively. This makes these coals less than desirable for electrical utilities, the largest consumers of Kansas coals. These utilities are looking to low sulfur, low ash subbituminous coal fields in the Western states as sources of clean feedstock. Kansas coals have the advantage, however, of producing 50% more heat from washed coal than an equal volume of western coal (Brady and Dutcher, 1973).

The relatively high sulfur and ash contents of Kansas coals prevent unrestricted combustion in power or steam generating facilities. Exposure to ash particulates and the detrimental effects of $SO_2$ in the atmosphere require some restriction on their use. Stack gas clean-up using scrubbers

and filters to remove sulfur and ash products adds a significant burden to the generation process. An alternative route would be to reduce the initial sulfur and ash content of the feedstock coal before combustion. This would lower overall plant load and insure reduced emissions of $SO_2$ and particulates. Coal liquefaction via a hydrogen donor solvent provides such an alternative.

Liquefaction Fundamentals

Bituminous coal is believed to be composed of a lattice work of carbon atoms, present primarily in groups of 3 to 5 condensed aromatic nuclei, which are joined together by aliphatic bonds consisting of methylene, disulfide, ether, or thioether linkages. Nitrogen, oxygen, and sulfur may also appear in the lattice positions (Wiser et al., 1971; Shalabi et al., 1979). It is these short-chain bonds which are fractured above 360°C (633 K). Guin (1976) found that coal mixed with a hydrogen donor solvent fragmented into smaller particles above 340°C (613 K). It was postulated that heat transfer from the solvent was the rate determining factor for a saturated coal particle. Application of heat alone was found to be insufficient for coal particle disintegration at 300-400°C (573-673 K).

The thermal cleavage of coal linkage bonds produces two large free radical species. These free radicals are stabilized according to the available species in the immediate environment. If hydrogen is available either in the form of a hydrogen donating solvent, such as tetralin, or a hydrogen shuttler, such as naphthalene or pyridine, the free radical may form a lower molecular weight species than the original fragment. If the physical structure of the coal does not permit introduction of hydrogen, the fragments may repolymerize to form a hydrogen deficient polyaromatic structure similar to coke (Wiser et al., 1971; Shalabi et al., 1979). Neavel (1976) has shown that compounds within the coal may stabilize

the free radical segments to form lighter compounds, a process he calls autogeneous hydrogen transfer.

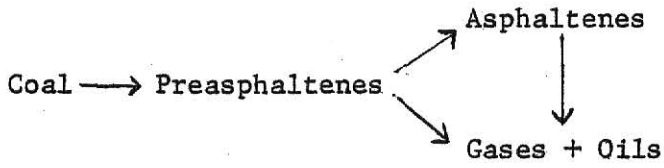
Coal liquefaction products are generally classified by their solubility or insolubility in various organic solvents. The division of products into four classes has been commonly used; unconverted coal and mineral matter, preasphaltenes or asphaltols, asphaltenes, and oils and gases (Neavel, 1976; Shalabi et al., 1979; Ruether, 1977; Guin et al., 1979; Given et al., 1975). Unconverted coal and mineral matter are insoluble in pyridine, quinoline, or tetrahydrofuran. Preasphaltenes are assumed to be benzene insoluble, but soluble in pyridine, quinoline, or tetrahydrofuran. Asphaltenes are insoluble in pentane or hexane but benzene soluble. Gases and oils are soluble in all the solvents used.

The solvents in such a separation scheme may be classified into three groups (Wise, 1971), based on their extractive powers on raw coal. Pentane, hexane, and benzene are non-specific solvents which show no dissolution of coal up to 127°C (400 K). Pyridine and quinoline are specific solvents which dissolve appreciable amounts of coal below 227°C (500 K) by a process of physical dissolution. Tetralin and tetrahydrofuran are reactive solvents which may react chemically with the coal, donating hydrogen as they convert to naphthalene and furan. Osafune (1976b) reported a dissolution of 90% of the organic matter in a Japanese coal washed in quinoline at 390°C (663 K), for one hour. Application of a solvent separation scheme must attribute dissolutions to the proper agent, liquefaction via a given process or the separation solvent itself.

Several investigators have proposed various reaction mechanisms for the conversion of coal to liquid and gaseous products in a hydrogen donor

solvent system (Cronauer et al., 1978; Shalabi et al., 1979). Three common models are given below.

$$\text{Coal} \longrightarrow \text{Preasphaltenes} \longrightarrow \text{Asphaltenes} \longrightarrow \text{Gases + Oils} \qquad (1)$$

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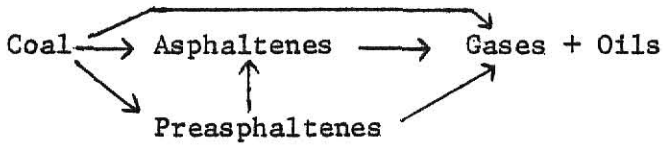


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Neavel (1976) suggested that the relatively complex interactions involving physical breakdown of the coal particles, thermally induced bond rupture rates, and competition between donor hydrogen stabilization and recombination of the free radical fragments make such simple reaction mechanisms unproductive in regards to understanding the actual chemical reaction mechanisms. Further process-variable studies, product-characterization procedures, and more meaningful coal characterization techniques must be developed before any useful reaction mechanisms can be arrived at.

Several investigators have observed the catalytic effect of minerals present in coal ash, such as sodium, potassium, iron, silicon, and aluminum, in the conversion of coal to gaseous and liquid products. Wright and Severson (1972) reacted anthracene oil with coal pyridine insolubles having a 46.1 wt. % ash content, in the presence of hydrogen gas. A second experiment involved reacting North Dakota lignite, carbon monoxide, water, anthracene oil and commercial sodium and iron catalysts together. In both cases the anthracene oil exhibited an increased hydrogen content, leading the experimenters to conclude that the coal minerals could promote

hydrogenation of the system donor solvent. Mukhurjee and Chowdhury (1976) separated a North Assam coal into various fractions by flotation. Reacting each fraction with hydrogen at 400°C (673 K), a pressure of 1400 psi ($9.65 \times 10^6$ Pa), for three hours, they observed that the conversion of coal to benzene solubles was enhanced by an increase in ash content. Guin and his coworkers (1978, 1979) reacted a Kentucky high volatile bituminous coal with creosote oil and recycled mineral matter at 425°C (698 K) and 2000 psi ($1.38 \times 10^7$ Pa), observing a rise in solvent hydrogenation with increased recycle. Coal ash was also studied as a catalyst for the hydrodesulfurization of model compounds such as phenyl sulfide and benzothiophene. Minerals which acted as sulfur scavengers increased hydrodesulfurization by lowering the partial pressure of $H_2S$, an inhibitant to sulfur removal from the coal. Apparently coal minerals may act as a catalyst to promote either solvent hydrogenation or dehydrogenation, depending on the hydrogen partial pressure in the system (Guin et al., 1978, 1979; Wright and Severson, 1972). The presence of coal minerals may or may not be desirable, depending on reaction conditions and process objectives.

Donor Solvent Liquefaction Processes

The two major hydrogen donor solvent liquefaction schemes currently under investigation in the United States are the Solvent Refined Coal process (SRC) and the Exxon Donor Solvent process (EDS). Both projects represent a joint funding effort between government and various industrial participants.

The SRC 50 ton per day pilot plant in Ft. Lewis, Washington is being operated by the Pittsburgh and Midway Coal Mining Company, a Kansas corporation which is a subsidiary of Gulf Oil Corporation, under the sponsorship

of the Department of Energy. The 6 ton per day SRC plant at Wilsonville, Alabama, is operated by Southern Company Services, Inc., under the joint sponsorship of DOE and the Electric Power Research Institute. An abbreviated flow sheet is shown in Figure 1. Pulverized coal is slurried with a process derived solvent, pumped to 1500-2000 psig ($1.03 \times 10^7$ - $1.38 \times 10^7$ Pa), mixed with hydrogen, and fed into a dissolver. A 30 minute residence time in the dissolver, at 427-468°C (700-740 K), results in dissolution of 93% of the carbonaceous material in the coal. The slurry is cracked and hydrogenated to produce lower molecular weight liquids and gases. Up to 60% of the organic sulfur is converted to $H_2S$. Light hydrocarbons, unused hydrogen, and $H_2S$ are flash-distilled from the heavy components in a separation vessel. The unreacted coal and mineral matter are separated from the heavy hydrocarbons by vacuum filtration in a rotary leaf filter. The filtrate is vacuum distilled to recover the process solvent, a middle distillate cut boiling at 177-287°C (450-560 K). The SRC I product has a solidification point of 177-204°C (450-478 K), and a heating value of approximately 16,000 BTU/lb ($3.72 \times 10^7$ J/kg).

The Ft. Lewis plant has been modified to allow recycle of a portion of the reactor effluent slurry for mixing with the pulverized coal feed. By increasing the reactor temperature and pressure the major product is changed from a solid to a liquid distillate having a boiling range of 177-454°C (450-728 K). The elemental distribution of the three major product cuts from the filtrate distillation system are shown in Table 1. The elemental H/C ratio increases from about 0.80, for a bituminous coal, to 0.97 for the heavy distillate, 1.24 for the middle distillate, and 1.73 for the naphtha cut. Overall product sulfur content ranges from 0.2-0.4%, and ash content from 0.06-0.16%. (Jimeson, 1976; Anon., 1978).

The Exxon Donor Solvent process (EDS) is currently being investigated in a 1 ton per day pilot plant in Baytown, Texas. A 250 ton per day plant which will provide the data necessary for scale-up to a 50,000 bbl/day commercial unit is under construction. An abbreviated flow sheet is shown in Figure 2.

In the EDS process coal is dried, crushed to -30 mesh, and slurried with a hydrogenated donor solvent and hydrogen. The mixture is reacted at 427 to 471°C (700-744 K), at 2200 psi ($1.50 \times 10^7$ Pa), for residence times of 15 to 140 minutes. Acid gas released during depressurization is cleaned and processed, returning hydrogen to the system. Unreacted coal, mineral matter, and components boiling above 540°C (813 K) are separated from the low boiling products via vacuum distillation at 370°C (643 K) and a pressure of 25 mm Hg ($3.29 \times 10^{-2}$ atm or $3.33 \times 10^3$ Pa). The overhead stream from the vacuum column is separated into a heavy gas oil product and a light gas oil. This light oil is rehydrogenated in a fixed bed catalytic reactor and fractionated to derive the process solvent cut. The solvent boiling range is typically 200∿450°C (473∿723 K). Overhead naphtha is used as a fuel gas for process heating needs. Solvent not used in the process recycle is mixed with the heavy vacuum oil to produce a low sulfur fuel oil. The product analysis for a typical run using Illinois coal is shown in Table 2. The elemental H/C ratio is increased from 0.86, for the Illinois bituminous coal, to 1.03 for the low sulfur fuel oil, and 1.52 for the heavy naphtha product. Overall sulfur content is reduced from 3.50%, in the wet feed coal, to 0.44% in the final product (Furlong et al., 1976; Anon., 1979).

The Kyushu-Koshi Solvolysis process has been investigated at the Government Industrial Research Institute, in Kyushu, Japan. Bench-scale

batch reactors are currently being used to investigate the effects of various process variables on the conversion of coal to gaseous and liquid products. The Kyushu-Koshi process differs from other liquefaction schemes in that coal dissolution takes place in a noncatalytic atmospheric system. A heavy petroleum product, such as vacuum residue or asphalt, is used as the process solvent. It is believed that thermal treating of the heavy solvent near 400°C (673 K) results in cracking of the long aliphatic bonds and subsequent polymerization to form ring and aromatic structures, thus making hydrogen available for transfer to the thermally induced coal free radical fragments.

The solvolysis process is fairly coal specific with reported conversions of solid coal to quinoline soluble liquid and gaseous products as high as 90% for a Japanese coal having 83% carbon (Osafune et al., 1976a,b). This compares favorably with liquefaction processes operating at elevated pressures with commercial catalysts (Wen and Han, 1975). Other investigators, however, have reported lower conversions for other coals. Osafune (1976b) reported conversions of Miike coal reacted at 390°C (663 K) for one hour, of 28.7% based on benzene solubles, 52.6% based on pyridine solubles, and 71.2% based on quinoline solubles. Miike coal contains 7.5% ash on a dry basis, and has an elemental H/C ratio of 0.84. Yamada (1974) reacted a Miike B coal containing 7.4% ash, with an H/C ratio of 0.82, at 400°C (673 K), for one hour. He observed conversions of 10% based on benzene solubles and 30% based on quinoline solubles. Kruse (1976) reacted a Winrock coal at 431°C (704 K) and reported a conversion of 25.7% based on quinoline solubles. Winrock coal contains 4.1% ash on a dry basis, and has an H/C ratio of 0.82. The elemental composition of the major feed and products for Kruse's reaction (1976) are given in

Table 3. The solvolysis reaction produces a gas stream, a light oil condensate, and a coke-like residue, 29.8% of which is quinoline soluble in Kruse's reaction.

## CONCLUDING REMARKS

The Kyushu-Koshi solvolysis liquefaction process may provide a suitable route for the elimination of the high ash and sulfur content of raw Kansas coals. A clean boiler fuel may result from such a process. The high ash content of Kansas coals may enhance the conversion of Kansas coals to gaseous and liquid products.

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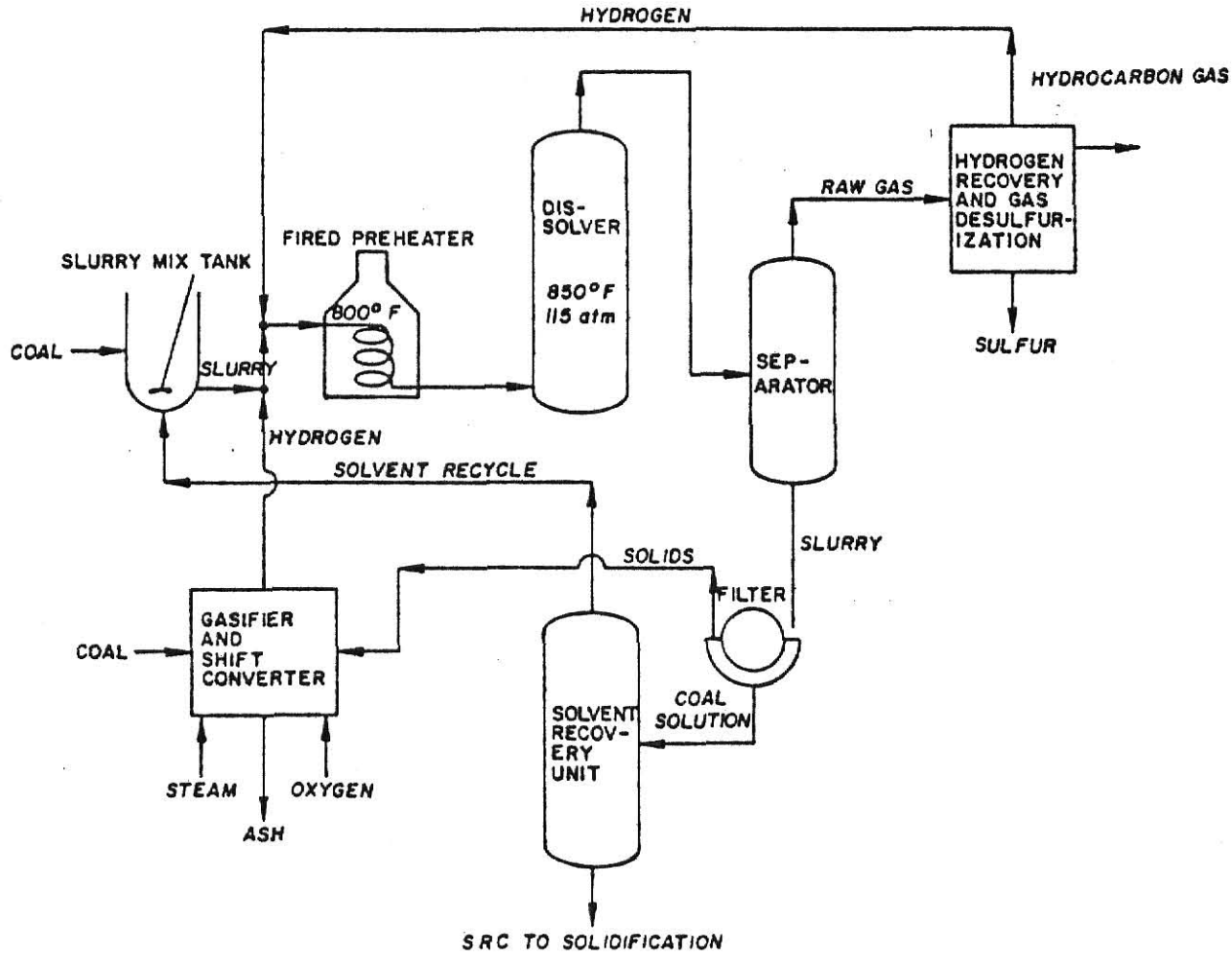


Figure 1. SRC Flowsheet (Anon., 1978)

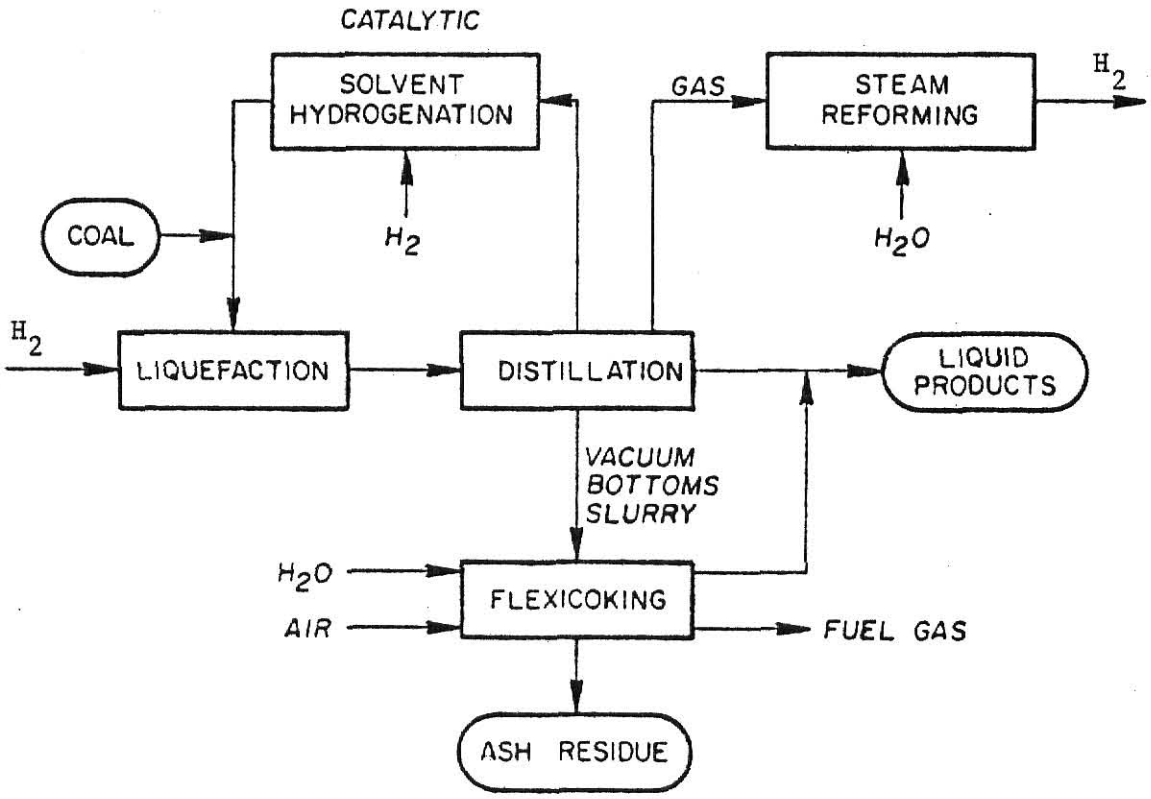


Figure 2. EDS Flowsheet (Anon., 1979).

Table 1. SRC Liquid Product Composition
(Anon., 1978)

| Element | Naphtha Wt. % | Middle Distillate Wt. % | Heavy Distillate Wt. % |
|---|---|---|---|
| Carbon | 85.17 | 87.03 | 87.18 |
| Hydrogen | 12.38 | 8.69 | 7.30 |
| Nitrogen | 0.52 | 0.98 | 1.17 |
| Sulfur | 0.27 | 0.21 | 0.53 |
| Oxygen | 1.66 | 3.09 | 3.82 |
| | 100.00 | 100.00 | 100.00 |

Table 2. EDS Liquid Product Composition
(Furlong, et al., 1976)

| Element | Heavy Naphtha Wt. % | 200°C + Fuel Oil Wt. % |
|---|---|---|
| Carbon | 85.60 | 89.40 |
| Hydrogen | 10.90 | 7.70 |
| Nitrogen | 0.21 | 0.66 |
| Sulfur | 0.47 | 0.41 |
| Oxygen | 2.82 | 1.83 |
| | 100.00 | 100.00 |

Table 3. Data from Kruse (1976); Stream Elemental Composition

| Component | Winrock Coal In Wt. % | Phillips Asphalt In Wt. % | Gas Out (Air, $O_2$, & $N_2$ Free) Wt. % | Oil Condensate Out Wt. % | Coke-Like Residue Wt. % |
|---|---|---|---|---|---|
| Carbon | 78.72 | 85.84 | 79.33 | 84.01 | 81.40 |
| Hydrogen | 5.42 | 10.20 | 19.57 | 13.30 | 5.37 |
| Nitrogen | 1.97 | 0.53 | ——— | 0.08 | 2.31 |
| Sulfur | 0.72 | 3.20 | 1.09 | 1.54 | 1.42 |
| Oxygen | 7.28 | 0.23 | ——— | 1.07 | 3.22 |
| Moisture | 1.86 | 0.00 | ——— | 0.00 | 1.23 |
| Ash | 4.02 | 0.00 | ——— | 0.00 | 5.04 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

# CHAPTER III

# SOLVOLYSIS LIQUEFACTION OF A KANSAS COAL

## An Experimental Study

## INTRODUCTION

Increased environmental restriction of sulfur and ash emissions is forcing electric utilities, the largest consumers of Kansas coals, to seek low ash and sulfur feedstocks from the Wyoming subbituminous coal fields. Kansas coals are relatively high in ash (10-35 wt.%) and sulfur content (2.6-5.0 wt.%). A coal liquefaction process could remove the limitations of high ash and sulfur content by providing a suitably clean feedstock for public utilities, thereby increasing the demand for Kansas coals.

The Kyushu-Koshi solvolysis liquefaction process (Honda and Yamada, 1974a, b) involves atmospheric noncatalytic dissolution of coal in a heavy solvent such as vacuum residue, coal tar or asphalt. When coal is heated above 350°C (623 K), disintegration of the coal structure is said to yield free radical fragments which are stabilized according to the species available in the immediate environment (Wiser et al., 1971). The free radical fragments may repolymerize to form a heavy molecular component or utilize a hydrogen atom donated from an appropriate solvent to form a gaseous or liquid compound. It has been proposed that thermal treating of the solvent near 400°C (673 K) results in cracking of the long aliphatic bonds and subsequent polymerization to form ring and aromatic structures, thus providing hydrogen for transfer to the coal free radicals (Honda and Yamada, 1974a; Sanada, 1972; Sanada et al., 1975).

The solvolysis process is fairly coal specific with reported conversions of solid coal to quinoline soluble liquid and gaseous products as high as 90% for a Japanese coal having 82-83% carbon (Osafune et al., 1976a,b). This compares favorably with liquefaction processes operating at elevated pressures with commercial catalysts (Wen and Han, 1975). Other investigators, however, have reported lower conversions for other coals. Osafune (1976b)

reported conversions of 28.7% based on benzene solubles, 52.6% based on pyridine solubles, and 71.2% based on quinoline solubles, reacting a Miike coal at 390°C (663 K) for one hour. At 400°C (673 K), Yamada (1974) reported conversions of 10% based on benzene solubles, and 30% based on quinoline solubles. Kruse (1976) found a conversion of 25.7% based on quinoline solubles, at 431°C (704 K). Hsu and Fan (1978) observed a maximum conversion of 23%, based on benzene solubles, when reacting a Texas lignite at 380°C (653 K), for 30 minutes.

The main objective of this study was to determine the applicability of the Kyushu-Koshi solvolysis liquefaction process to a major Kansas coal, Baxter coal, by observing the behavior of a bench-scale batch reactor over a range of system parameters; reaction temperature, 380-400°C (653-693 K), reaction time, 0-90 minutes, and a solvent-to-coal weight ratio of 1:1 - 2:1.

## EXPERIMENTAL

This section includes a listing of the experimental equipment, materials, materials preparation, experimental procedure, and analysis procedures used in the solvolysis liquefaction of Baxter coal, a Kansas coal.

### Equipment

The liquefaction equipment is shown in Figure 1. It consisted of a Glas-Col heating mantle rated at 600 watts, with the maximum temperature of 650°C (923 K), a Love Controls model 49-869 PID temperature controller fitted with a type J iron/constantan thermocouple, a constant speed control unit coupled to a stirrer motor, a Honeywell Electronik 19 chart recorder, and glassware, consisting of a 1000 ml three-necked flask, an anchor-type stirrer, an air-cooled reflux column, a water-cooled condenser, a condensate collection flask, and various connecting pieces. Auxiliary equipment included a Quaker City Mill grinder, Model 4-E, a Burrows Equipment Company sample splitter, a Ro-Tap Sieve Shaker, Model B, a Soxhlet extractor, a Thermolyne Type 1500 furnace, a Gelman pressure filter equipped with a glass filter element, and a Packard gas chromatograph.

### Materials and Preparation

Approximately 100 lbs (45 kg) of Baxter coal, also called Mineral coal, were obtained from the Clemens Coal Company Mine #22, located near Mulberry, Kansas, in Crawford County. Raw coal was transported in airtight plastic bags, ground to pass a 50 mesh sieve (0.0117 in. or $2.97 \times 10^{-4}$ m), run through the splitter to insure sample uniformity, and stored in 1000 ml plastic bottles. A five gallon sample of an 85/100 penetration asphalt was obtained from the Phillips Petroleum Company. ACS grade benzene and quinoline were used as separation solvents.

Procedure

Approximately 0.10 kg of Baxter coal and 0.10~0.20 kg of Phillips asphalt were charged into the reaction flask. After wrapping the vessel with asbestos insulating tape, the slurry was heated from an initial temperature of about 50°C (323 K) to the desired reaction temperature of 380~420°C (653~693 K). This initial heat-up took approximately 15 minutes. The stirrer was operated at 100 rpm once the slurry reached 100°C (373 K). A record of the vessel temperature was provided via output from the temperature controller to the chart recorder.

Reaction time zero was taken as the point when the desired reaction temperature was reached. Gases and light oils generated by the reaction slurry passed through the vertical reflux column and the condenser into the ice-bath cooled collection flask, trapping the liquids. Gases were vented into the fume hood. Unreacted coal, mineral matter, and high boiling oils and tars remained as a slurry in the reaction flask. At the end of the appropriate reaction time, the asbestos strips were removed. and the slurry was allowed to cool. Benzene was added to the hardened slurry to dissolve the heavy oil component. The benzene insolubles were washed in the Soxhlet extractor for 24 hours to remove any traces of heavy oil product. The remaining solids were dried at 105°C (378 K), weighed, and ashed. An ash balance was made on the system by the following equation.

Deviation in Ash Balance in %

$$= 100 \times \frac{\text{(Ash in with reactants)} - \text{(Ash out with products)}}{\text{(Ash in with reactants)}} \qquad (1)$$

Any balance which deviated by more than $\pm$ 10% was rejected. Heavy oil product weight was determined as follows:

Heavy Oil Product Weight

= (Slurry weight at the end of reaction) - (Dry washed solids weight) (2)

Light oil product was trapped and weighed in the collection flask. Gas product was determined by difference according to the following expression:

$$\text{Gas Product Weight} = (\text{Reactant weight}) - (\text{Heavy oil weight}) - (\text{Light oil weight}) - (\text{Dry solids weight}) \quad (3)$$

The degree of conversion of coal to gaseous and liquid products was measured by the percent reduction of dry ash-free (DAF) solids, as shown below:

$$\%\ \text{Reduction of DAF solids} = \frac{\left[(\text{Coal wt.}) \times (100 - \text{Ash \%} - \text{Moisture \%}) - (\text{Dry solids wt.}) \times (100 - \text{Solids ash \%})\right]}{(\text{Coal wt.}) \times (100 - \text{Ash \%} - \text{Moisture \%})} \times 100 \quad (4)$$

A 100% reduction in DAF solids would represent conversion of all the organic matter present in the coal to benzene soluble products. A negative percent reduction of DAF solids may result when heavy oils in the reaction slurry are coked to become benzene insolubles. If enough coking takes place during the reaction, more organic benzene insoluble matter will be present in the products than was initially contained in the reactants.

Supporting Analysis

Moisture and ash analyses of the raw coal and benzene insoluble solids were performed according to ASTM Standards D3173-73 and D3174-73, respectively. An elemental analysis of the four major product streams was made at three representative reaction conditions. Two gas samples from each run were analyzed on the gas chromatograph, using a molecular sieve column to identify $H_2$, $O_2$, $N_2$, $CH_4$, and CO, and a Porapak column to identify $CO_2$, $C_2H_4$, $C_2H_6$, $C_3H_6$, $C_3H_8$, $H_2O$, and $H_2S$. Light oil product was analyzed by Hauser Laboratories of Boulder, Colorado. Baxter coal, Phillips asphalt, heavy oil product, and benzene insoluble solids were analyzed by Hazen Research, Inc., of Golden, Colorado. Liquid and solid

stream analyses were given as weight percent carbon, hydrogen, nitrogen, sulfur, and ash, with oxygen determined by difference.

Separation Solvents

The separation solvents used in the classification of coal liquefaction product streams vary in their power to dissolve various compounds. In order to study the effect of quinoline and benzene on Baxter coal, a 0.10 kg sample of coal was washed in the Soxhlet extractor for 24 hours. The undissolved solids were dried and weighed in the same manner as the solid products from the solvolysis reaction. The dissolution power of the solvents was determined by calculating the percent reduction of DAF solids in each case.

## RESULTS AND DISCUSSION

The effects of reaction time, temperature, and solvent-to-coal weight ratio on the conversion of Baxter coal to gaseous and liquid products using the Kyushu-Koshi solvolysis liquefaction process were determined by examining the percent reduction of dry ash-free (DAF) solids [Equation (1)], and the product distribution on a cumulative weight percent basis. The four major product streams were defined as gases, light oils condensed from the overhead stream, heavy oils or asphaltenes remaining in the reaction vessel, and solids composed of benzene insoluble organic matter and ash.

### Effect of Reaction Time

The coal and asphalt reactants were mixed for about 15 minutes before the slurry reached the appropriate reaction temperature, where the reaction time was taken to be zero. Over the temperature range 380-420°C (653-693 K) a 10-15% reduction of DAF solids resulted from this initial heat-up period. At 380°C (653 K) solids reduction increased with reaction time, plateauing from 45 to 90 minutes. At any reaction time an increase in the solvent-to-coal ratio resulted in greater percent solids reduction. Figure 2 presents the results of experiments conducted at 400°C (673 K), where a maximum in the percent reduction of DAF solids was observed at about 30 minutes. A decrease in percent solids reduction with time followed the maximum, with lower solvent-to-coal ratios producing a sharper decline. Conversion of asphaltenes to benzene insoluble organic matter resulted in a negative percent reduction of DAF solids. At 420°C (693 K) the percent reduction of solids fell monotonically with increasing reaction time. After 45 minutes all reactions produced benzene insolubles from asphalt coking. At extended times and elevated temperatures reproducibility became increasingly difficult due to coking problems in the system. Several runs

could not be performed because the reactants formed a solid mass in the reaction vessel making stirring and temperature maintenance impossible.

Figure 3 shows the distribution of gases, light oils, heavy oils, and solids on a cumulative weight percent basis, at 400°C (673 K). Benzene insoluble solids decreased slightly from 0 to 30 minutes, and then grew with increasing reaction time. Gas and light oil production rose with time to a combined total of approximately 15% at 90 minutes. At 380°C (653 K) no significant quantities of light oil were produced. Weight percent gases increased and weight percent solids decreased with time for all solvent-to-coal ratios. At 420°C (693 K) gases, light oils, and solids all increased with time as heavy oils were cracked to yield gases and light oils, and coked to give benzene insoluble organic matter. Up to 25% of the total products appeared as gases and light oils at a reaction time of 90 minutes.

Effect of Reaction Temperature

The reaction temperature of the reaction slurry showed a marked effect on the percent reduction of DAF solids. At a reaction time of zero minutes, solids reduction increased from 9% at 380°C (653 K) to 17% at 420°C (693 K) for solvent-to-coal ratios of 1.5:1 and 2:1 respectively. Figure 4 shows that at a reaction time of 30 minutes the reduction of DAF solids rose from 12∿22% at 380°C (653 K), to 16∿25% at 400°C (673 K), falling rapidly to 3∿9% at 420°C (693 K), as coking of asphaltenes to benzene insolubles developed. Figure 5 presents the effects of extended reaction times and elevated temperatures, which acted together to promote coking. At reaction times greater than 60 minutes and temperatures in excess of 400°C (673 K), the undesirable solids production dominated.

The effect of temperature on product distribution is shown in Figure 6. Below 380°C (653 K) essentially no light oils were produced. Gas production rose slightly with temperature while light oils increased rapidly above 400°C (673). The weight percent of solids grew with temperature, rising sharply at temperatures above 400°C (673 K), as coking of the heavy asphaltenes was enhanced.

The catalytic effect of coal on coke production from asphaltenes may be seen in Figure 7. The product distribution of asphalt-coal experiments at different temperatures is compared to runs conducted using an asphalt-inert system. No coke formation was observed when only inert solids were present. When coal was present, however, benzene insoluble organic matter was produced from the asphaltene portion of the reactants, along with an increase in gases and light oils. This suggests that the combination of high temperatures and increased ash contents may be detrimental to the conversion of coal to gaseous and liquid products in the Kyushu-Koshi process.

Effect of Solvent-to-Coal Weight Ratio

Reduction of DAF solids generally was enhanced by an increase in the solvent-to-coal ratio over the range between 1:1 and 2:1. At 380°C (653 K) solids reduction increased from 8∿14% at a ratio of 1:1 to 10∿23% at a ratio of 2:1. Increased reaction times yielded larger reduction of DAF solids. Figure 8 shows the effect of solvent-to-coal ratio at 400°C (673 K). All reaction times showed a rise in solids reduction with increased solvent-to-coal ratio. An inversion effect is seen at 400°C (673 K), however, with intermediate reaction times giving the greatest reduction of DAF solids. At 90 minutes coking resulted in the least reduction of the four reaction times investigated. At 420°C (693 K) solids

reduction rose with the solvent-to-coal ratio, with increasing reaction times yielding lower overall percent reduction of DAF solids.

Figure 9 presents the effect of solvent-to-coal ratio over the range 1:1 to 5:1, for a reaction time of 30 minutes. There appears to be no significant gain in solids reduction above a weight ratio of 3:1. A trade off between process solvent load and percent reduction of DAF solids would lead to an optimum solvent-to-coal ratio for a fully developed system. It appears that a 30% reduction of DAF solids represents the practical maximum in the application of the Kyushu-Koshi solvolysis process to the conversion of Baxter coal to benzene soluble gases and liquids.

Figure 10 shows the effect of solvent-to-coal weight ratio on product distribution. Gas and light oil weight percents decreased slightly with increasing solvent-to-coal ratio. Solids declined according to the proportion of coal charged to the system. A solvent-to-coal ratio of 1:1 represented 50% coal by weight, 1.5:1 - 40% coal, 2:1 - 33.3% coal, and 5:1 - 16.7% coal. Since the amount of solids charged to the system decreased with the solvent-to-coal ratio, percent reduction of DAF solids represents a more accurate indicator of the conversion than measuring only the weight percent of benzene insolubles present.

Since much of the gas and light oil product was assumed to originate in the asphalt portion of the reactants, an increase in solvent charge would be expected to increase the amounts of gas and oil produced. Figure 11 shows the gas and light oil production normalized on an asphalt basis. If these products came solely from the asphalt any solvent-to-coal ratio should yield the same proportion of gases and light oils given a reaction time and temperature. Figure 12 shows that a better fit was obtained by normalizing with respect to the total reactants charged, asphalt

plus coal. This suggests that the products are the result of an interaction between coal and solvent rather than being produced from simple asphalt cracking and distillation.

Stream Analysis

The reactant and product streams for three different reaction conditions were analyzed to determine the change in elemental distribution as a result of the solvolysis process. The elemental stream compositions at 400°C (673 K), a solvent-to-coal ratio of 1:1, and a reaction time of 30 minutes (400-1:1-30), are shown in Table 1. The other two conditions investigated were 380-2:1-60, and 420-1.5:1-60. The elemental H/C ratio of the benzene insoluble solids varied from 0.82 at 380°C (653 K), to 0.71 at 420°C (693 K), the increased carbon apparently coming from coked asphaltenes. Heavy oil carbon and hydrogen composition was closely related to that of the original asphalt for all three conditions, appearing to be independent of temperature, time, or solvent-to-coal weight ratio. Asphalt H/C elemental ratio was 1.49, heavy oil H/C ratio was $1.40 \pm 0.03$. No light oils were produced at 380°C (653 K). The light oil composition was approximately the same at 400 and 420°C (673 and 693 K), with an H/C ratio of $1.81 \pm 0.01$.

The gas stream composition varied widely for the three reaction conditions. During each reaction two gas samples were taken for analysis. The results suggest that the gas composition is essentially independent of time. The correlation of gas and light oil production to the amount of total reactants charged (Figure 12) suggests that gas stream composition would depend to a greater degree on reaction temperature than on the solvent-to-coal ratio. Figure 13 presents the change in major gas constituents with respect to temperature. Alkanes and $H_2$ production increased,

while relative production of $H_2S$ decreased, as the reaction temperature rose from 380°C (653 K) to 420°C (693 K). Levels of CO, $CO_2$, and alkenes remained approximately constant below 5 volume percent.

The elemental distribution of carbon, hydrogen, nitrogen, sulfur, oxygen, and ash, among the input and output streams at 400°C (673 K) is shown in Table 2. The relative amounts of carbon, nitrogen, and ash present in the solids and heavy oils were closely related to the initial distribution between coal and asphalt. The distribution of hydrogen, sulfur, and oxygen was strongly affected by the specific reaction conditions.

As reaction temperature increased, gas and light oil production rose. This shifted the amount of total system hydrogen present in the gas and light oil streams from 4% at 380°C (653 K), to over 33% at 420°C (693 K). Nitrogen was concentrated in the solids, rising from 42% to 73% as temperature increased. Total system sulfur in the gases and light oils ranged from 30% to 45%. Sulfur present in the benzene insoluble solids rose from 27% at 380°C (653 K), to 50% at 420°C (693 K).

Elemental balances were made for all three reaction conditions. Carbon balances closed to within 0.6%, hydrogen balances closed to within 5%, and ash balances closed to within 7%. Sulfur, nitrogen and oxygen balances closed within an average of 40%.

The loss of system hydrogen in the gas and light oil streams explains the coking of heavy oils to produce benzene insolubles. As gas and light oil production increased, the partial pressure of hydrogen became too low to promote efficient hydrogen transfer to the free radicals formed by thermal cracking in the coal. This resulted in repolymerization within the coal and coking of the heavy oil asphaltenes to produce an increase in benzene insoluble solids. The reduced effectiveness of the available

system hydrogen is the main disadvantage of the atmospheric liquefaction system.

Separation Solvent Effect

To determine the effect of various separation solvents a sample of coal was ashed in the extractor using benzene or quinoline. Benzene produced only a 2% reduction in DAF solids, while quinoline reduced DAF solids by 32.5%. Each experiment was conducted at the atmospheric boiling point of the respective solvent, 80°C (353 K) for benzene, and 273°C (510 K) for quinoline. Osafune, et al. (1976b), reported a reduction in DAF solids of 0% for benzene and 90.4% for quinoline, using a Japanese coal washed at 390°C (663 K) for one hour. These results suggest that the use of quinoline, or other powerful solvents, in classifying product streams may mask the true effects of the solvolysis process. Reported conversions of coals to gases and liquids in excess of 30% may be due to the dissolving power of the separation solvent rather than the dissolution of coal by the hydrogen transfer from the heavy residuum solvent in the solvolysis liquefaction reaction.

## CONCLUSIONS

Several conclusions may be drawn from the experimental application of the Kyushu-Koshi solvolysis process in the conversion of Baxter coal to gaseous and liquid products. The catalytic effect of coal in converting heavy asphaltenes to gas and light oil products competes with the liquefaction of coal via hydrogen transfer to the thermally induced free radicals. The low partial pressure of hydrogen promotes coking of the heavy oils, producing benzene insolubles, an undesirable product.

An optimum reaction time of 30 minutes gives the maximum reduction of DAF solids of 25% at 400 $^{o}$C (673 K), and a solvent-to-coal weight ratio of 2:1. An optimum solvent-to-coal ratio exists due to the competing factors of system solvent load and percent reduction of DAF solids. This optimum solids reduction compares well with the 10% conversion reported by Yamada (1974) at 400 $^{o}$C (673 K), the 28.7% conversion reported by Osafune (1976b) at 390 $^{o}$C (653 K), and the 25.7% conversion observed by Kruse (1976) at 431 $^{o}$C (704 K). Apparently Baxter coal has no special characteristics which would promote an unusually high conversion to liquid products in the Kyushu-Koshi process.

Great care should be exercised when classifying product streams to insure that the conversion of coal to desirable products is attributed to the correct agent. Powerful separation solvents may mask the true efficiency of a particular liquefaction process.

The efficiency of the solvolysis process could be improved in several ways. First, recycling of the hydrogen-rich gases and light oils to the reaction mixture, second, operating the reaction vessel at pressures above one atmosphere, and third, reacting the slurry under a blanket of hydrogen gas. All of these steps would increase the partial pressure of hydrogen in the reaction vessel, promoting the formation of liquid products.

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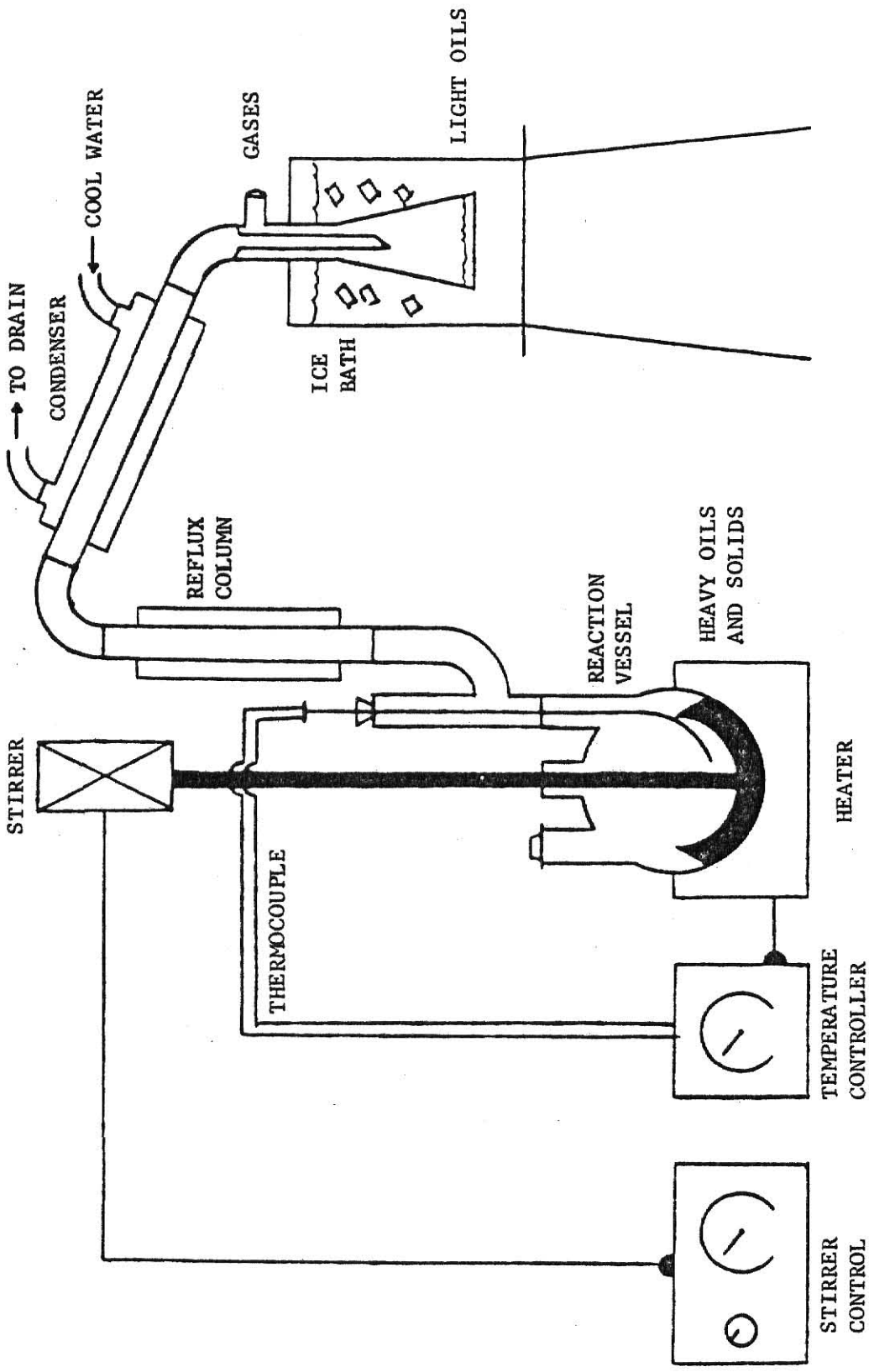


Figure 1. Experimental equipment.

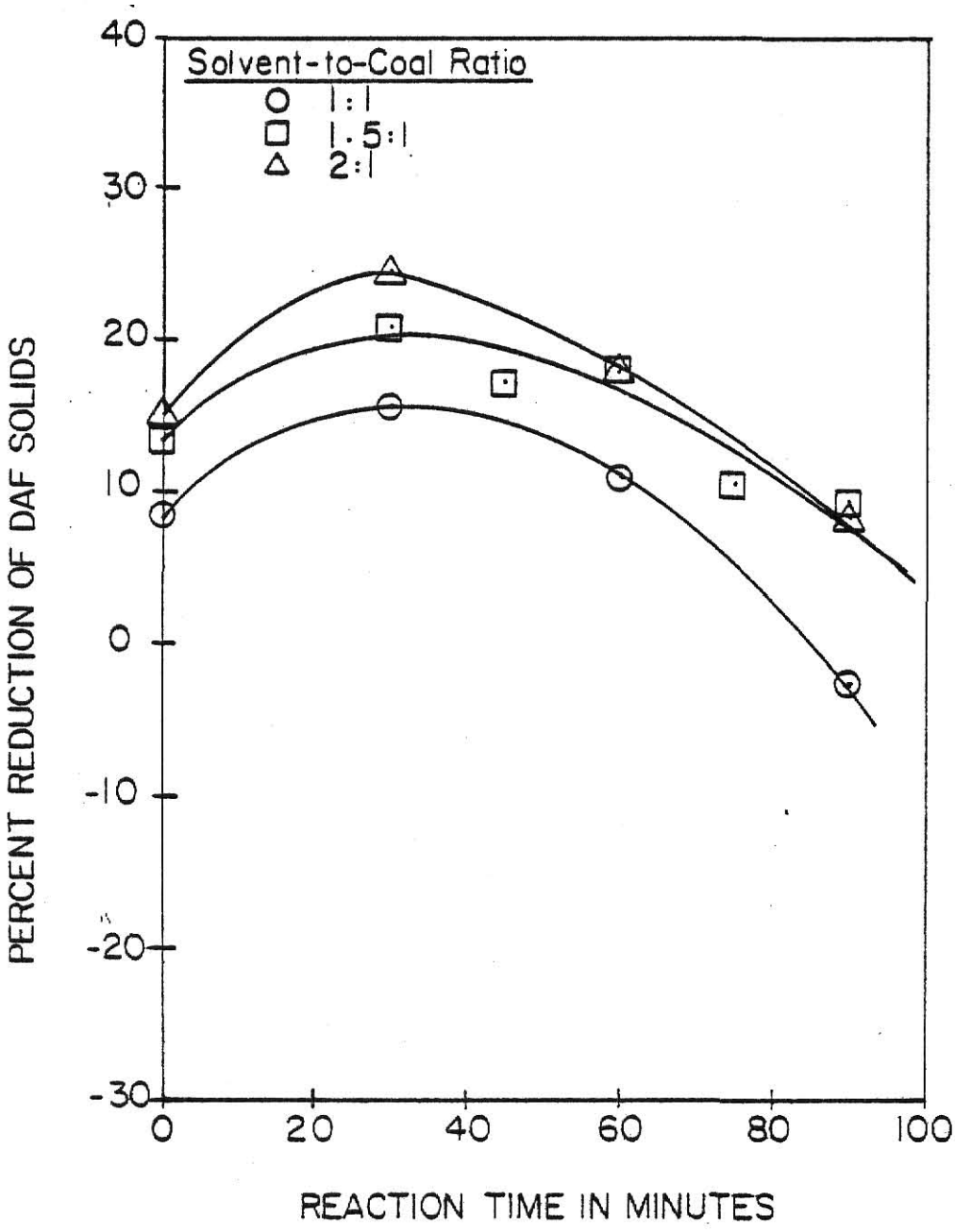


Figure 2. Effect of reaction time on solids reduction:

Temperature = 400 °C (673 K)

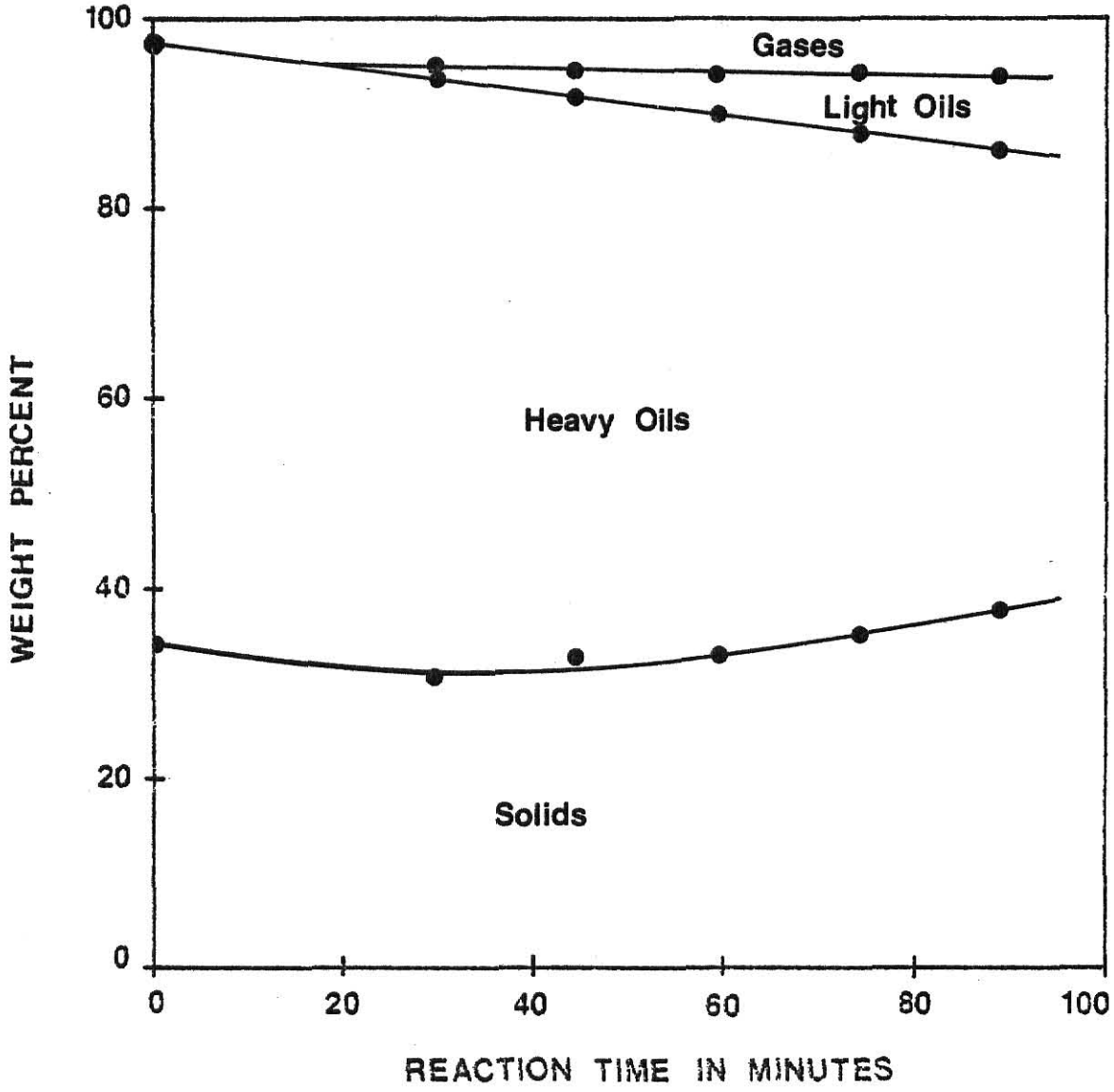


Figure 3. Effect of reaction time on product distribution:

Temperature = 400 °C (673 K)
Solvent-to-Coal ratio = 1.5:1

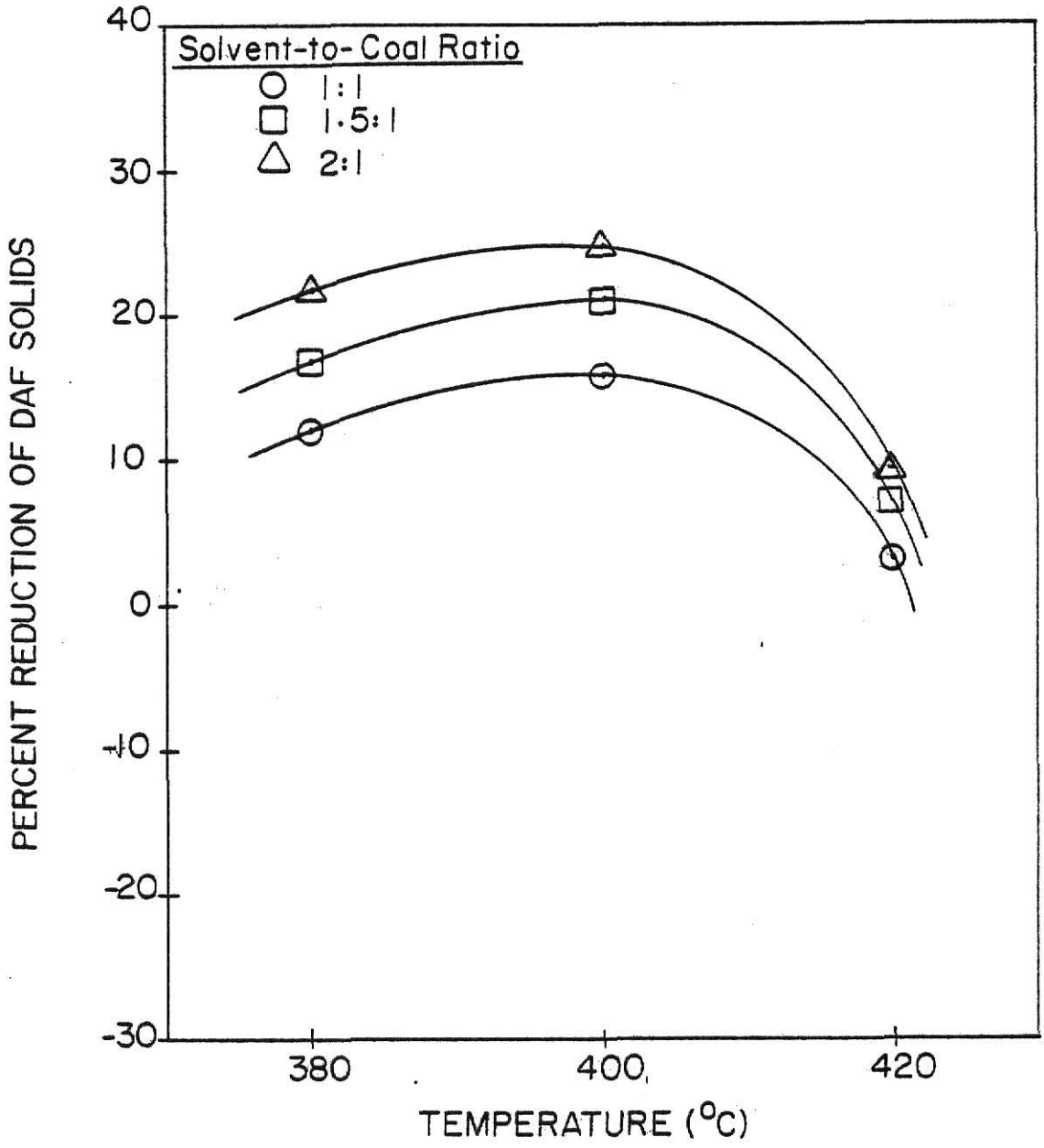


Figure 4. Effect of reaction temperature on solids reduction:

Time = 30 minutes.

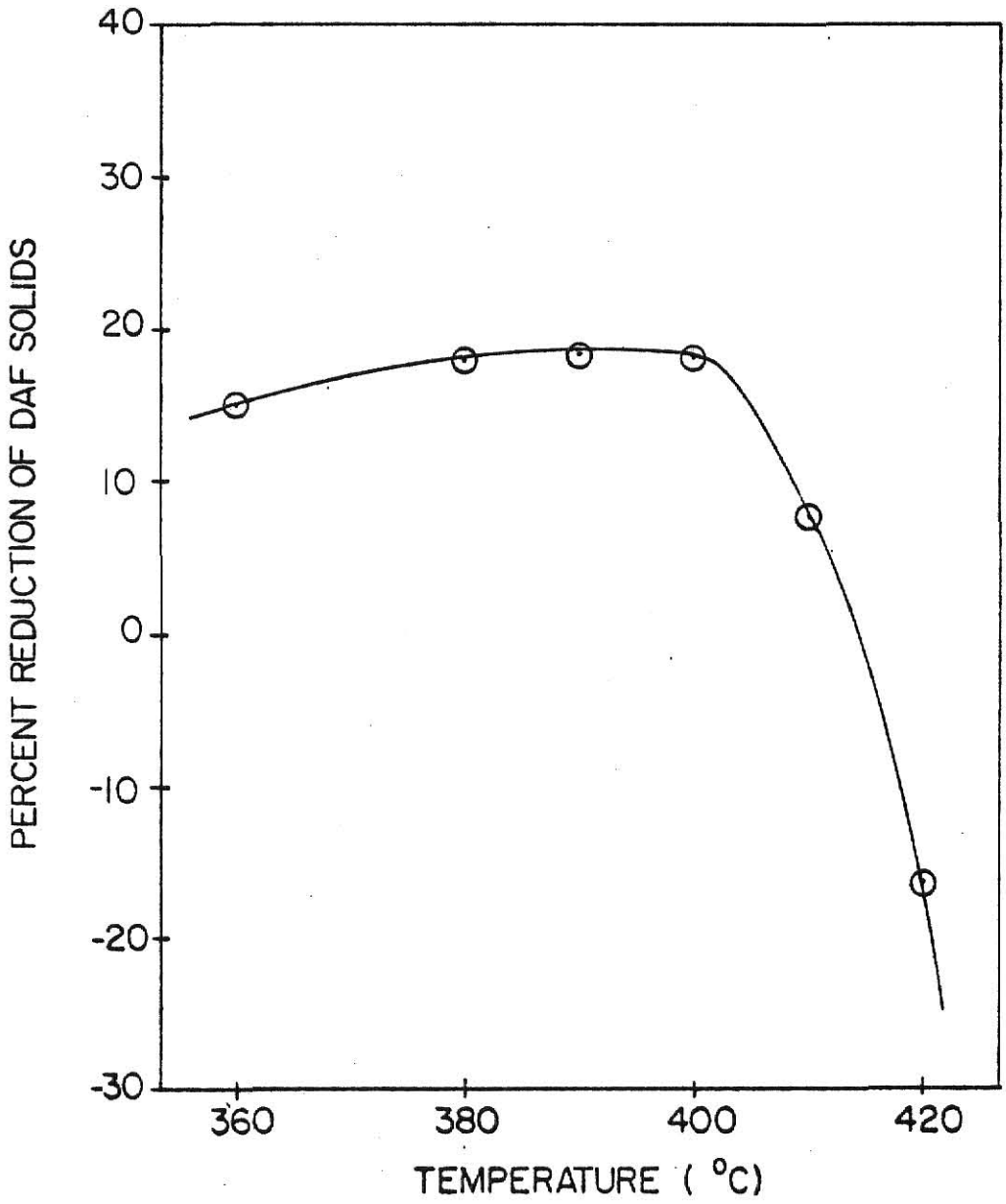


Figure 5. Effect of reaction temperature on solids reduction:

Time = 60 minutes
Solvent-to-Coal ratio = 1.5:1.

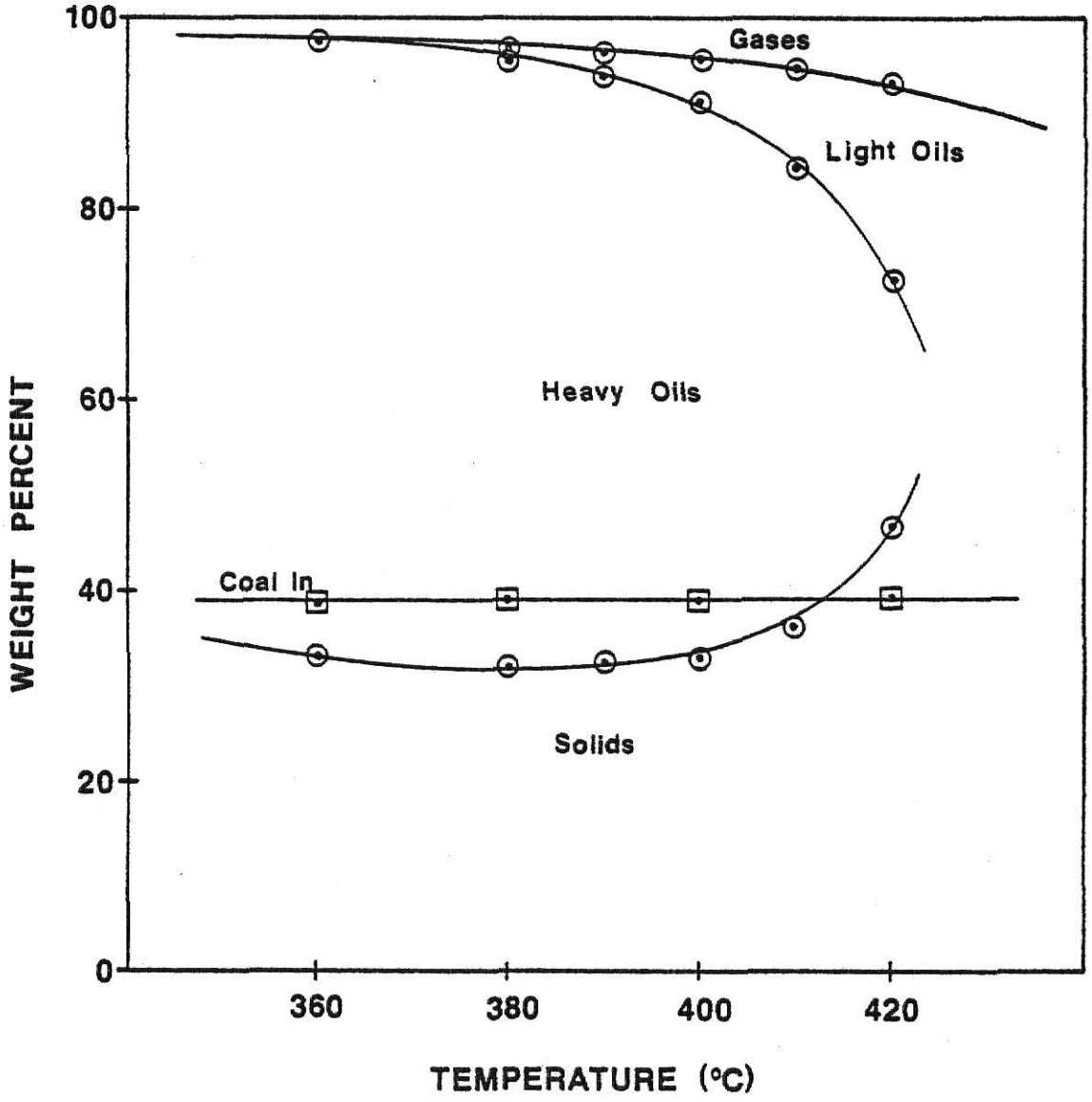


Figure 6. Effect of reaction temperature on product distribution:

Time = 60 minutes
Solvent-to-Coal ratio = 1.5:1.

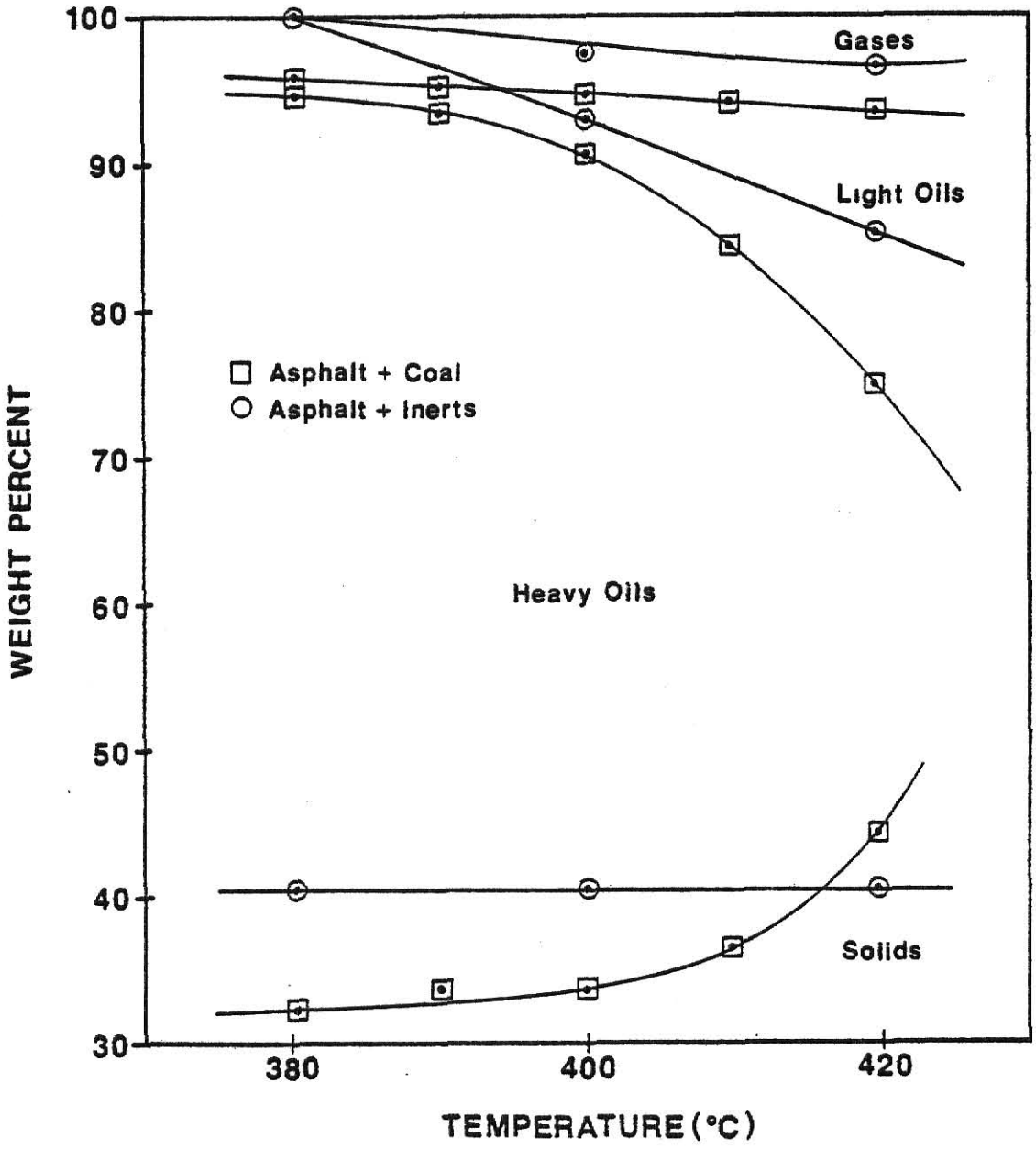


Figure 7. Effect of coal on product distribution:

Time = 60 minutes
Solvent-to-Coal ratio = 1.5:1.

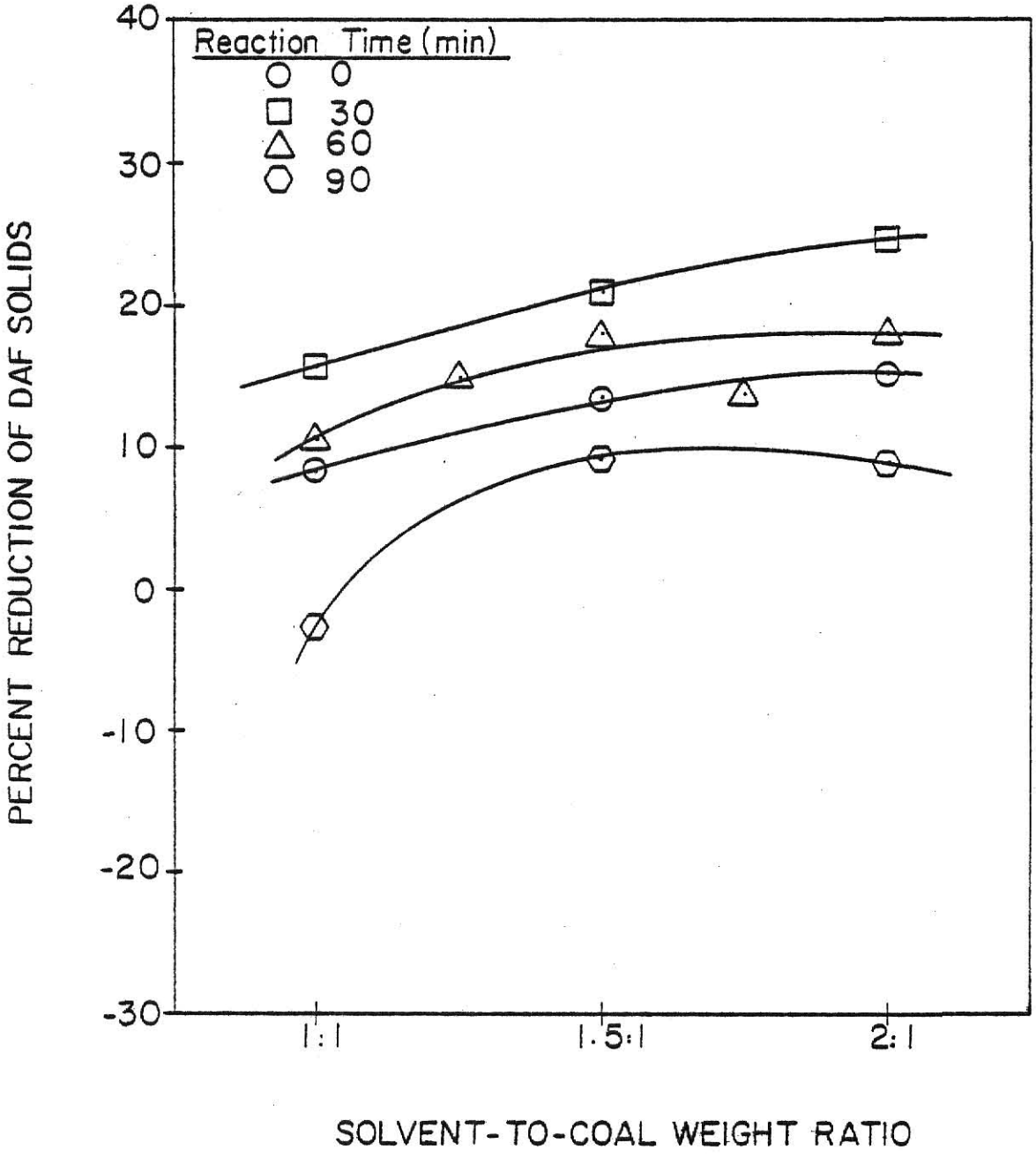


Figure 8. Effect of solvent-to-coal ratio on solids reduction:

Temperature = 400 °C (673 K).

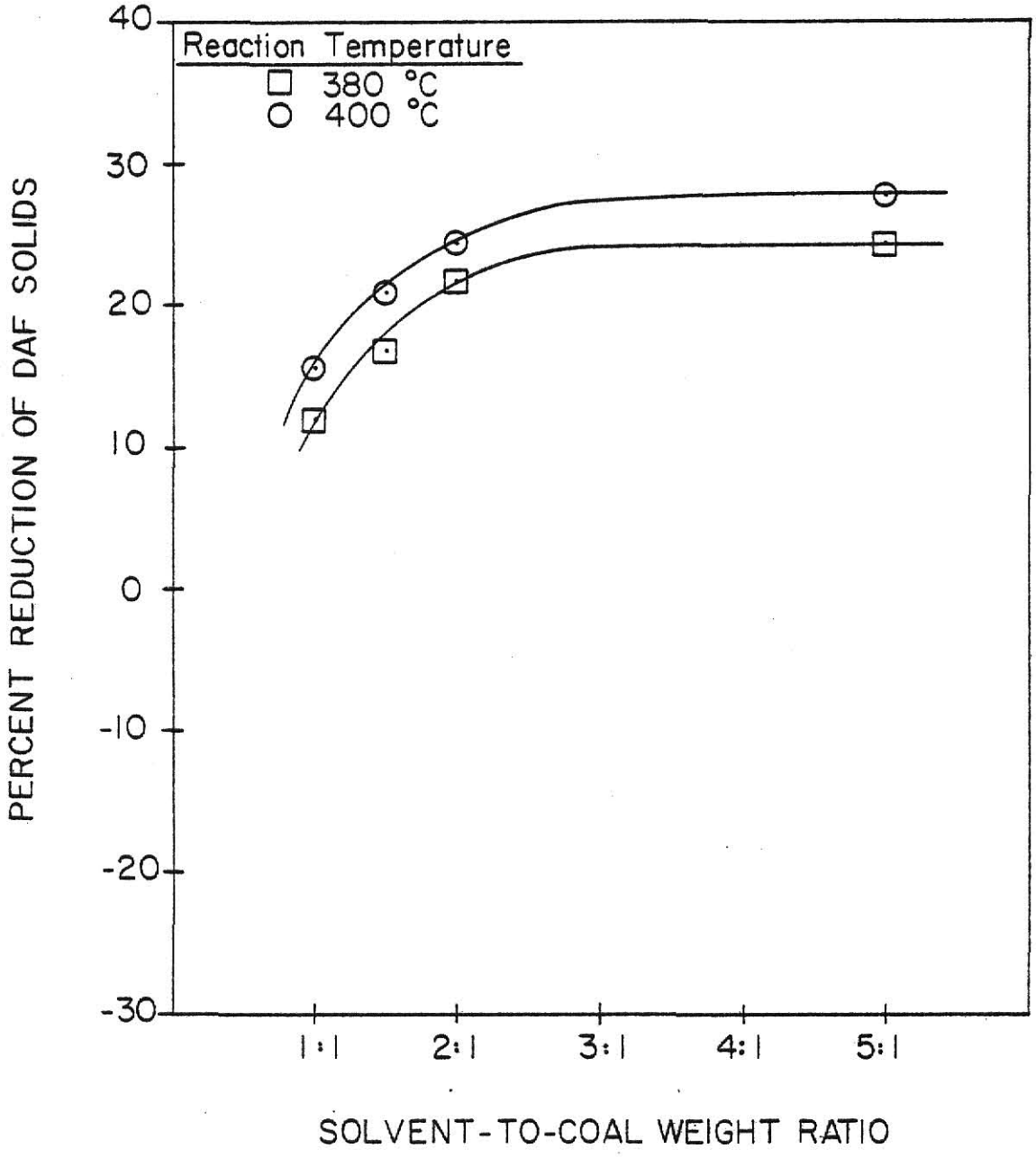


Figure 9. Effect of solvent-to-coal ratio on solids reduction:

Time = 30 minutes.

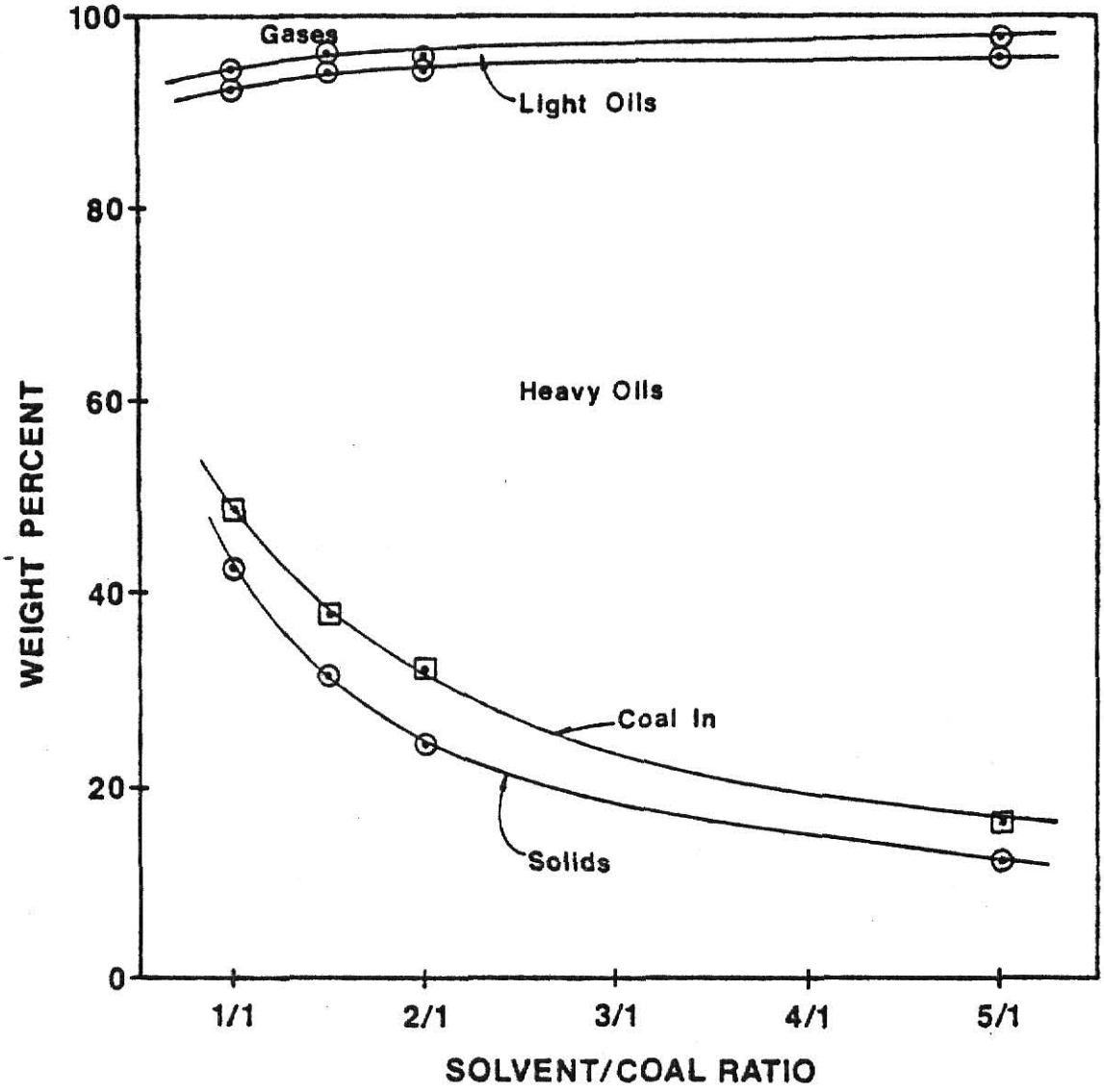


Figure 10. Effect of solvent-to-coal ratio on product distribution:

Temperature = 400 °C (673 K)
Time = 30 minutes.

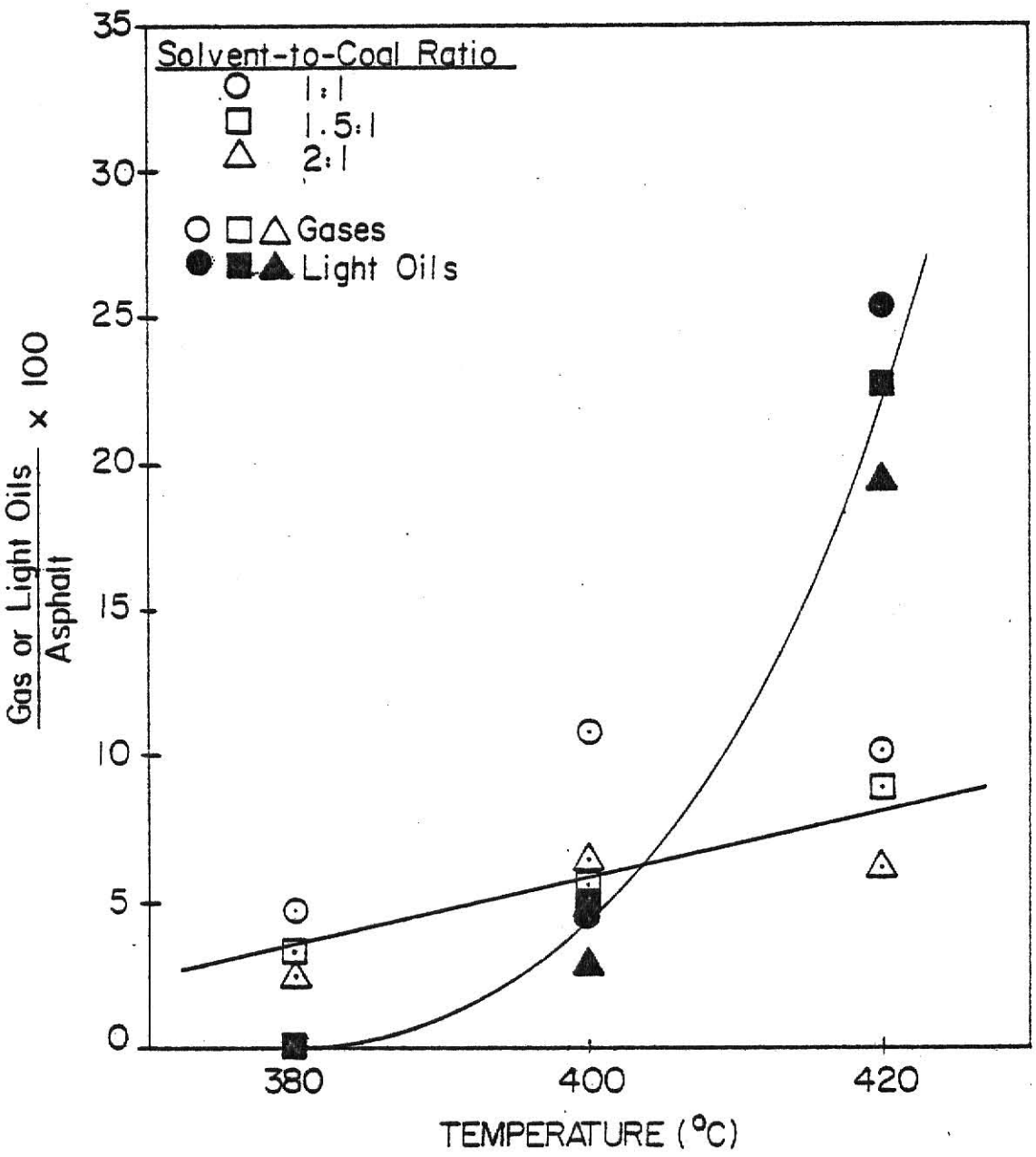


Figure 11. Proportional amounts of gases and light oils produced based on asphalt charged:

Time = 30 minutes.

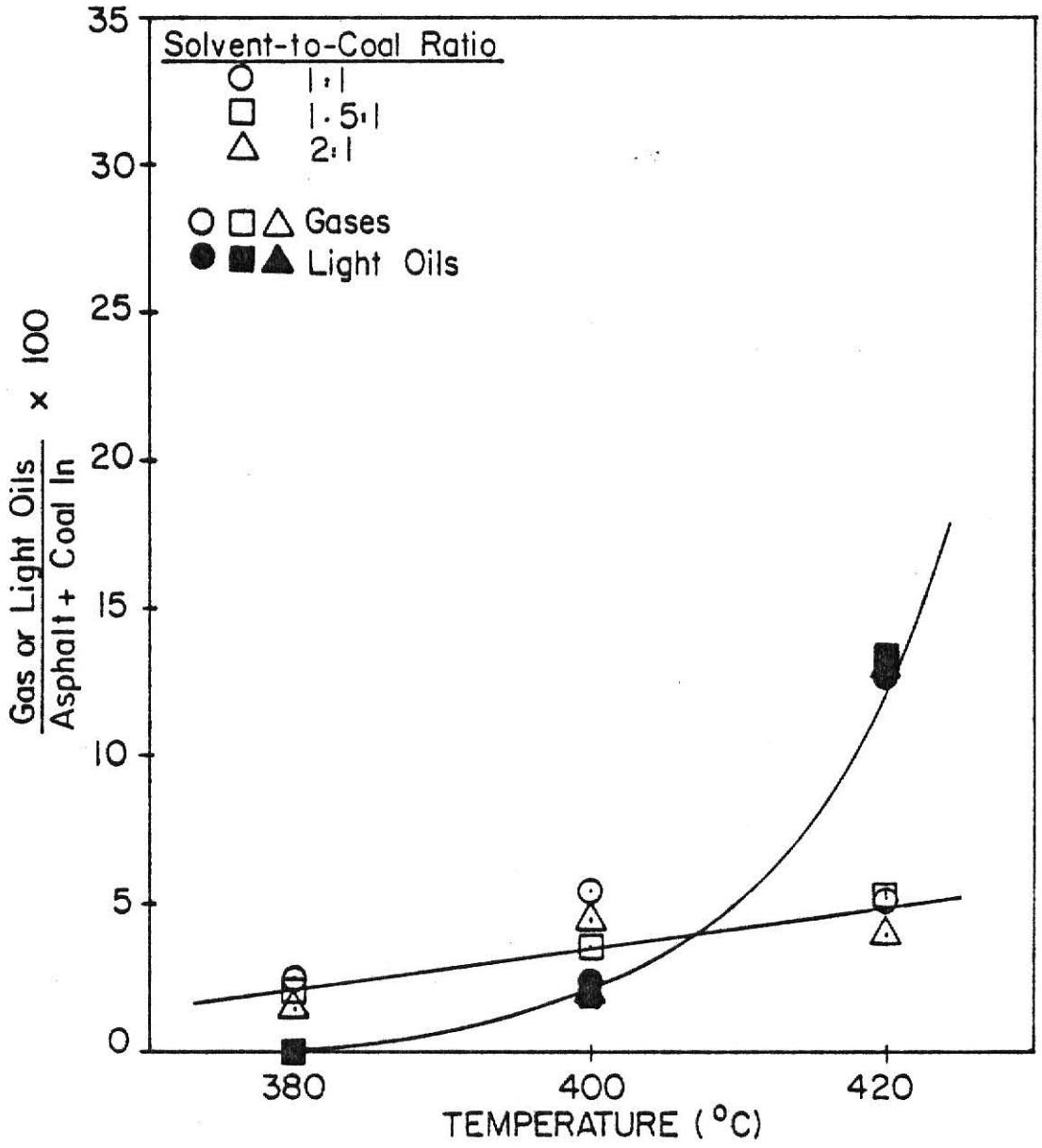


Figure 12. Proportional amounts of gases and light oils produced based on coal and asphalt charged:

Time = 30 minutes.

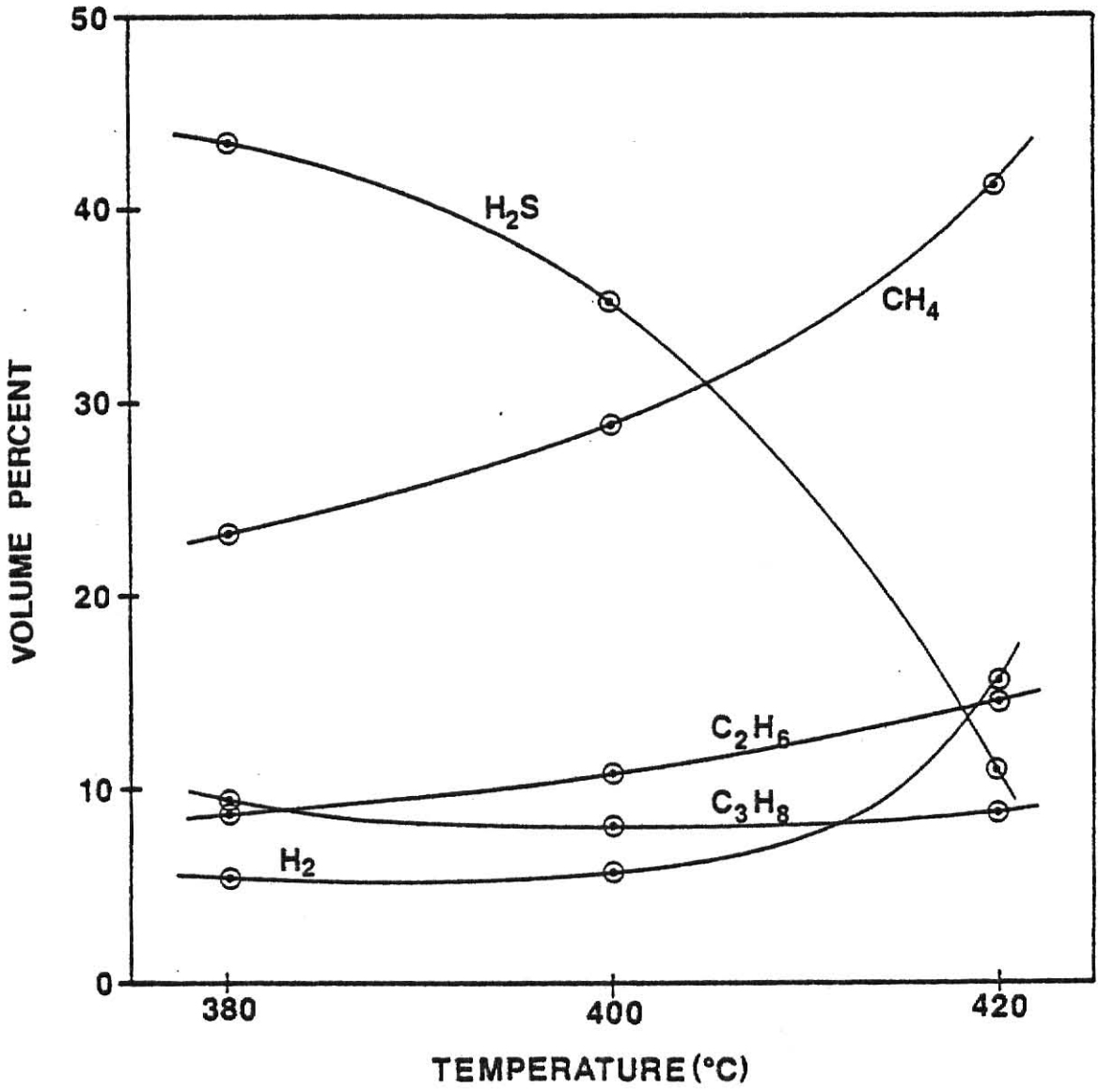


Figure 13. Major gas stream components:

380-(2:1)-60

400-(1:1)-30

420-(1.5:1)-60.

Table 1. Stream Composition

Temperature = 400°C (673 K)
Time = 30 minutes
Solvent-to-Coal = 1:1

| Component | Coal In Wt. % | Asphalt In Wt. % | Gases Out Wt. % | Light Oils Out Wt. % | Heavy Oils Out Wt. % | Solids Out Wt. % |
|---|---|---|---|---|---|---|
| Carbon | 61.26 | 85.68 | 41.01 | 85.61 | 86.29 | 61.28 |
| Hydrogen | 4.50 | 10.73 | 12.89 | 12.96 | 9.88 | 4.20 |
| Nitrogen | 1.07 | 0.19 | 0.00 | 0.12 | 0.80 | 1.60 |
| Sulfur | 4.55 | 2.21 | 41.32 | 1.26 | 1.87 | 4.27 |
| Oxygen | 6.27 | 1.06 | 4.78 | 0.05 | 1.09 | 2.77 |
| Ash | 22.35 | 0.13 | 0.00 | 0.00 | 0.07 | 25.88 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

Table 2. Elemental Distribution:

Temperature = 400°C (673 K)
Time = 30 minutes
Solvent-to-Coal = 1:1

| | % Carbon | % Hydrogen | % Nitrogen | % Sulfur | % Oxygen | % Ash |
|---|---|---|---|---|---|---|
| Input | | | | | | |
| Coal | 41.81 | 29.65 | 84.92 | 67.46 | 85.56 | 99.42 |
| Asphalt | 58.19 | 70.35 | 15.08 | 32.54 | 14.44 | 0.58 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| Output | | | | | | |
| Gases | 3.12 | 9.33 | 0.00 | 45.18 | 13.28 | 0.00 |
| Light Oils | 2.35 | 3.39 | 0.00 | 0.49 | 0.00 | 0.00 |
| Heavy Oils | 58.47 | 63.73 | 36.57 | 18.21 | 27.07 | 0.31 |
| Solids | 36.06 | 23.43 | 63.43 | 36.12 | 59.65 | 99.69 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

# CHAPTER IV

# SOLVOLYSIS LIQUEFACTION OF FOUR KANSAS COALS

## The Effect of Ash Content

## INTRODUCTION

Kansas electrical utilities are being forced by increasing environmental restrictions on sulfur and ash emissions to seek cleaner feedstocks. A coal liquefaction process could reduce the relatively high ash (10-35 wt.%) and sulfur content (2.6-5.0 wt.%) of Kansas coals, increasing their desirability.

The Kyushu-Koshi solvolysis liquefaction process involves noncatalytic dissolution of coal in a heavy solvent, such as asphalt, which is thermally treated near 400°C (673 K), cracking the long aliphatic bonds, to produce hydrogen donating ring and aromatic structures. Coal free radicals formed above 350°C (623 K) by thermal disintegration may stabilize by using this available hydrogen to form gaseous and liquid products (Honda and Yamada, 1974a, b; Wiser et al., 1971; Sanada, 1972; Sanada et al., 1975).

Conversions of coal to quinoline soluble liquid and gaseous products have been reported as high as 90% for a Japanese coal having 82-83% carbon (Osafune et al., 1976a,b). This compares favorably with liquefaction processes operating at elevated pressures with commercial catalysts (Wen and Han, 1975). Lower conversions have been observed with other coals. Osafune (1976b) reported conversions of Miike coal, containing 7.5% ash, of 28.7% based on benzene solubles, 52.6% based on pyridine solubles, and 71.2% based on quinoline solubles, when reacted at 390°C (663 K) for one hour. Yamada (1974) observed a conversion of 10% based on benzene solubles when reacting a similar Miike coal at 400°C (673 K). Kruse (1976) reacted a Winrock coal containing 4.1% ash at 431°C (704 K) and reported a conversion of 25.7% based on quinoline solubles.

Several investigators have observed the catalytic effect of minerals present in coal ash, such as sodium, potassium, iron, silicon, and aluminum,

in the conversion of coal to gaseous and liquid products. Wright and Severson (1972) reacted anthracene oil with coal pyridine insolubles having a 46.1% ash content, in the presence of gaseous hydrogen. A second experiment involved reacting North Dakota lignite, carbon monoxide, water, anthracene oil, and commercial sodium and iron catalysts together. In both cases the anthracene oil exhibited an increased hydrogen content, leading the experimenters to conclude that the coal minerals could promote hydrogenation of the system donor solvent. Mukhurjee and Chowdhury (1976) separated a North Assam coal into various fractions by flotation. Reacting each fraction with hydrogen at 400°C (673 K), a pressure of 1400 psi ($9.65 \times 10^6$ Pa), for three hours, they observed that the conversion of coal to benzene solubles was promoted by an increase in ash content. Guin and his coworkers (1978, 1979) reacted a Kentucky high volatile bituminous coal with creosote oil and recycled mineral matter at 425°C (698 K) and 2000 psi ($1.38 \times 10^7$ Pa), observing a rise in solvent hydrogenation with increased recycle. Coal ash was also studied as a catalyst for the hydrodesulfurization of model compounds such as phenyl sulfide and benzothiophene. Minerals which acted as sulfur scavengers increased hydrodesulfurization by lowering the partial pressure of $H_2S$, an inhibitant to sulfur removal from the coal. Apparently coal minerals may act catalytically to promote either solvent hydrogenation or dehydrogenation, depending on the hydrogen partial pressure in the system (Guin, 1978, 1979; Wright and Severson, 1972). The presence of coal minerals may or may not be desirable, depending on reaction conditions and process objectives.

The main objective of this study was to determine the effect of the ash content of four Kansas coals on the conversion to gaseous and liquid products using the Kyushu-Koshi solvolysis liquefaction process.

## EXPERIMENTAL

This section includes a listing of the experimental equipment, materials, materials preparation, experimental procedure, and analysis procedures, used in the solvolysis liquefaction of four Kansas coals.

### Equipment

The liquefaction equipment is shown in Figure 1. It consisted of a Glas-Col heating mantle rated at 600 watts, with the maximum temperature of 650°C (923 K), a Love Controls model 49-869 PID temperature controller fitted with a type J iron/constantan thermocouple, a constant speed control unit coupled to a stirring meter, a Honeywell Electronik 19 chart recorder, and glassware, consisting of a 1000 ml three-necked flask, an anchor-type stirrer, an air-cooled reflux column, a water-cooled condenser, a condensate collection flask, and various connecting pieces. Auxiliary equipment included a Quaker City Mill grinder, Model 4-E, a Burrows Equipment Company sample splitter, a Ro-Tap Sieve Shaker, Model B, a Soxhlet extractor, and a Thermolyne Type 1500 furnace.

### Materials and Preparation

Rowe coal was obtained from the Wilkinson Mine in Cherokee County, Baxter coal was obtained from the Clemens Coal Company Mine #22, in Crawford County, Mulberry coal was obtained from the Pittsburg and Midway Mine in Linn County, and Bevier coal was obtained from a supply stock present at the Kansas State University Department of Chemical Engineering. All four coals are bituminous, with Rowe, Baxter, and Bevier originating in the Cherokee Group formation, and Mulberry coming from the Marmaton Group formation. Raw coal was transported in airtight bags, ground to pass a 50 mesh sieve (0.0117 in. or $2.97 \times 10^{-4}$ m), run through a sample splitter to insure sample uniformity, and stored in 1000 ml plastic bottles. A five

gallon sample of an 85/100 penetration asphalt was obtained from the Phillips Petroleum Company. ACS grade benzene was used as a separation solvent.

Procedure

Approximately 0.10 kg of coal and 0.10-0.20 kg of Phillips asphalt were charged into the reaction flask. After wrapping the vessel with asbestos insulating tape the slurry was heated from an initial temperature of about 50°C (323 K) to the desired reaction temperature of 380∿420°C (653∿693 K). This initial heat-up took approximately 15 minutes. The stirrer was operated at 100 rpm once the slurry reached 100°C (373 K). A record of the vessel temperature was provided via output from the temperature controller to the chart recorder.

Reaction time zero was taken as the point when the desired reaction temperature was reached. Gases and light oils generated by the reaction slurry passed through the vertical reflux column and the condenser, into the ice-bath cooled collection flask, trapping the liquids. Gases were vented into the fume hood. Unreacted coal, mineral matter, and high boiling oils and tars remained as a slurry in the reaction flask. At the end of the appropriate reaction time, the asbestos strips were removed and the slurry was allowed to cool. Benzene was added to the hardened slurry to dissolve the heavy oil component. The benzene insolubles were washed in the Soxhlet extractor for 24 hours to remove any traces of heavy oil product. The remaining solids were dried at 105°C (378 K), weighed, and ashed. An ash balance was made on the system using the following expression:

$$\text{Deviation in Ash Balance \%} = 100 \times \frac{(\text{Ash in with reactants}) - (\text{Ash out with products})}{(\text{Ash in with reactants})} \qquad (1)$$

Any balance which deviated by more than ± 10% was rejected. Heavy oil product weight was determined as follows:

Heavy Oil Product Weight

= (Slurry weight at end of reaction) - (Dry solids wt.) (2)

Light oil product was trapped and weighed in the collection flask. Gas product weight was determined by the following equation:

Gas Product Weight = (Reactant weight) - (Heavy oil weight) (3)

- (Light oil weight) - (Dry solids weight)

The degree of conversion of coal to gaseous and liquid products was measured by the percent reduction of dry ash-free (DAF) solids, as shown below:

% Reduction of DAF Solds

$$= \frac{\text{(Coal wt.)x(100 - Ash \% - Moisture \%)} - \text{(Dry solids wt.)x(100 - Solids ash \%)}}{\text{(Coal wt.)x(100 - Ash \% - Moisture \%)}} \times 100 \quad (4)$$

A 100% reduction in DAF solids would represent conversion of all the organic matter present in the coal to benzene soluble products. A negative percent reduction of DAF solids may result when heavy oils in the reaction slurry are coked to become benzene insolubles. If enough coking takes place during the reaction, more organic benzene insoluble matter will be present in the products than was initially contained in the reactants.

Supporting Analysis

Moisture and ash analyses of the raw coal and benzene insolubles were performed according to ASTM Standards D3173-73 and D3174-73, respectively. Coal and asphalt samples were analyzed by Hazen Research, Inc., of Golden, Colorado. Elemental compositions were given as weight percent carbon, hydrogen, nitrogen, sulfur, ans ash, with oxygen determined by difference.

## RESULTS AND DISCUSSION

The effect of ash content on the conversion of four Kansas coals to gaseous and liquid products using the Kyushu-Koshi solvolysis liquefaction process was determined by examining the percent reduction of dry ash-free (DAF) solids [Equation (1)], and the product distribution on a cumulative weight percent basis. The major product streams were defined as gases, light oils condensed from the overhead stream, heavy oils or asphaltenes remaining in the reaction vessel, and solids composed of benzene insoluble organic matter and ash.

The compositions of the four bituminous Kansas coals used in this study are given in Tables 1, 2, 3, and 4. Ash content on a wet basis ranged from 13.9% for Bevier coal, to 32.6% for Mulberry coal. On a dry ash-free basis, the elemental weight percent of carbon ranged from 78.2 to 81.5%, that of hydrogen from 4.9 to 5.6%, that of nitrogen from 1.30 to 1.48%, that of sulfur from 6.0 to 7.6%, and that of oxygen from 4.70 to 8.96%. The elemental ratio of hydrogen to carbon (H/C) ranged from 0.711 for Rowe coal, to 0.826 for Bevier coal.

### Effect of Ash Content on Percent Reduction of DAF Solids

The effect of ash content on the percent reduction of DAF solids was observed at three representative reaction conditions. Figure 2 shows that at 380°C (653 K), a solvent-to-coal ratio of 2:1, and a reaction time of 60 minutes, reduction of DAF solids ranged from 13.0 to 22.7%. Solids reduction was enhanced by an increase in coal ash content up to approximately 23%. An ash content of 35.6%, on a dry basis, resulted in a lower percent reduction of solids than at 14.4 and 22.9% ash. Figure 3 presents the results at 400°C (673 K), a solvent-to-coal ratio of 1:1, and a reaction time of 30 minutes. Solids reduction ranged from 9.8 to 15.8%. An increase in ash content from 14.2 to 22.9% promoted the conversion of

organic matter to benzene soluble products. A minimum solids reduction occurred at 35.6% ash. Figure 4 shows the effect of ash content at 420°C (693 K), a solvent-to-coal ratio of 1.5:1, and a reaction time of 30 minutes. Reduction of DAF solids ranged from -6.6% at 35.6% ash, to 10.4% at 22.9%. The effect of ash content on solids reduction was similar to those at the lower temperature conditions.

The observed rise in percent reduction of DAF solids, and subsequent decrease, as ash content ranged from 14 to 36%, as shown in Figures 2, 3, and 4, may be explained as a combination of three factors. As ash content increased for a given solvent-to-coal ratio, the ratio of available solvent to organic matter present in the coal rose. For a solvent-to-coal ratio of 1.5:1 this ratio ranges from 1.78 at 13.9% ash, to 2.54 at 32.6% ash. An increase in the amount of solvent present has been shown to promote reduction of DAF solids in the case of Baxter coal (See Chapter III). A second factor affecting the percent reduction of DAF solids is the elemental ratio of hydrogen to carbon. Although Bevier and Rowe coals have similar ash contents, 14.4 and 14.2%, their H/C ratios are not equal. Rowe coal, with an H/C ratio of 0.71, exhibits a lower percent reduction of DAF solids at all three conditions than Bevier coal, which has an H/C ratio of 0.83. A coal with a higher H/C ratio would be expected to show a greater conversion to gaseous and liquid products given the same amount of available hydrogen donor solvent. A third factor influencing coal conversion behavior is the catalytic effect of coal mineral matter in the hydrogenation or dehydrogenation of donor solvents. All four Kansas coals contain some of the suspected catalytic minerals; Fe, $SiO_2$, $Fe_2O_3$, and FeS. In the Kyushu-Koshi solvolysis process the hydrogen-rich gas and light oil streams are allowed to exit from the system. The law of mass action, shown in Equation (5),

predicts solvent dehydrogenation, even to the point of transforming the asphaltic materials in the system to benzene insolubles.

$$\text{Hydrogen-Poor Solvent or Benzene Insolubles} + H_2(g) \xrightarrow{\text{Coal Minerals}} \text{Hydrogen-Rich Solvent or Benzene Solubles} \quad (5)$$

In general, as ash content increases, the effective solvent-to-organic matter ratio rises, promoting the conversion of coal, while catalytic dehydrogenation of the solvent also grows, yielding benzene insolubles. These combined effects give a maximum percent reduction of DAF solids for the four Kansas coals tested. The presence of a large amount of coal minerals in the Kyushu-Koshi process is undesirable due to the dehydrogenation of the solvent. Operating at atmospheric pressure, while allowing hydrogen-rich gas and light oil to leave the system, results in a decrease in the conversion of coal to benzene soluble products.

Effect of Ash Content on Product Distribution

The effect of coal ash content on the cumulative weight percent product distribution of four Kansas coals at three representative reaction conditions is presented in Figures 5, 6, and 7. The relative amounts of dry ash-free solids, heavy oils, light oils, and gases, are plotted on a cumulative basis versus the dry coal ash content.

Figure 5 shows the product distribution at 380°C (653 K), a solvent-to-coal ratio of 2:1, and a reaction time of 60 minutes. Gas production was approximately constant at 3-4 wt.%. Light oils accounted for about 1% of the total products. Total benzene insolubles decreased from 27.5 to 25.5%, as ash content rose from 14 to 23%. At 36% ash, total solids increased to 27%.

The product distribution at 400°C (673 K), a solvent-to-coal ratio of 1:1, and a reaction time of 30 minutes, is given in Figure 6. Gases

accounted for 5% of the total products. Light oil production ranged from 2% at 23% ash, to 9% at 36% ash. Total solids decreased from 44% at 14% ash, to 41% at 36% ash.

Figure 7 shows the product distribution at 420°C (693 K), a solvent-to-coal ratio of 1.5:1, and a reaction time of 30 minutes. Gas production was constant at about 5.5% for all four coals. Light oils accounted for approximately 15% of the total product weight. Benzene insolubles dropped from 40% to 35%, then rose to 39%, as ash content ranged from 14 to 36%.

The partial decline in benzene insoluble solids may be attributed to the relative increase in the solvent-to-organic matter ratio. This decrease is opposed by the catalytically enhanced dehydrogenation of asphaltenes to insoluble organic matter. The production of gases and light oils seems to be relatively independent of ash content. Factors such as the reaction conditions or initial coal hydrogen and oxygen contents affect the ultimate product distribution from the solvolysis reaction to a greater degree.

## CONCLUSIONS

The percent reduction of DAF solids and the product distribution resulting from the Kyushu-Koshi solvolysis process at any given reaction condition are affected by the ash content of the original coal and the ratio of asphaltene solvent to organic matter present in the coal. As ash content increases the rising proportion of solvent available to transfer hydrogen to the benzene insoluble organic portion of the reactants promotes a reduction in DAF solids. However, the increased amount of coal mineral matter present enhances the dehydrogenation of the asphaltic materials to benzene insoluble solids. These competing factors give rise to a maximum reduction of DAF solids at approximately 23% ash for the four Kansas coals tested. Gas and light oil production appear to be independent of ash content, but dependent on coal elemental H/C ratio and specific reaction conditions.

An increased ash content is detrimental to the conversion of coal to benzene soluble products using the atmospheric Kyushu-Koshi solvolysis process. The low partial pressure of hydrogen that results from gas venting promotes the catalytic dehydrogenation of the system solvent. This yields an increased production of benzene insolubles, an undesirable product.

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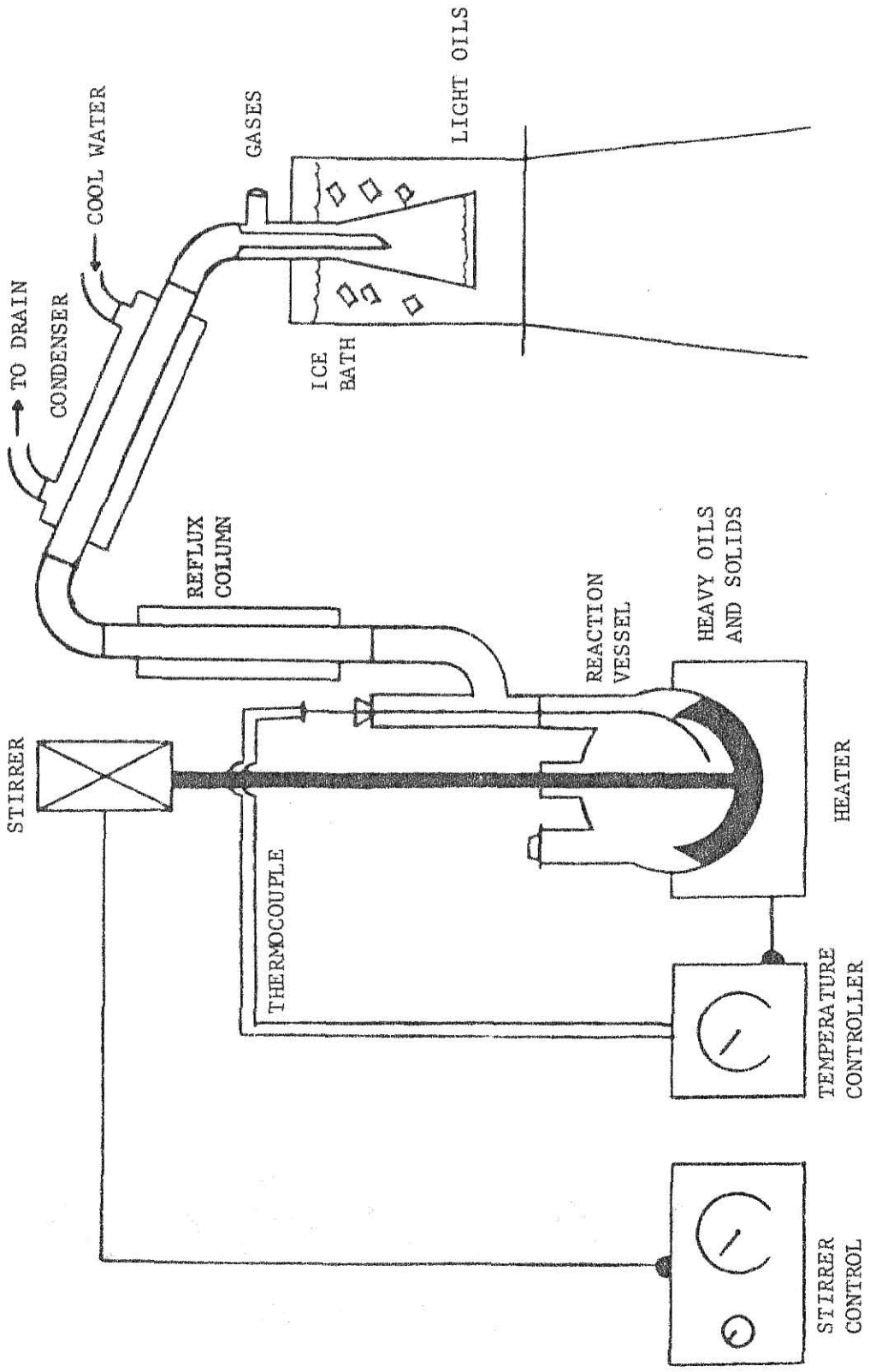


Figure 1. Experimental equipment.

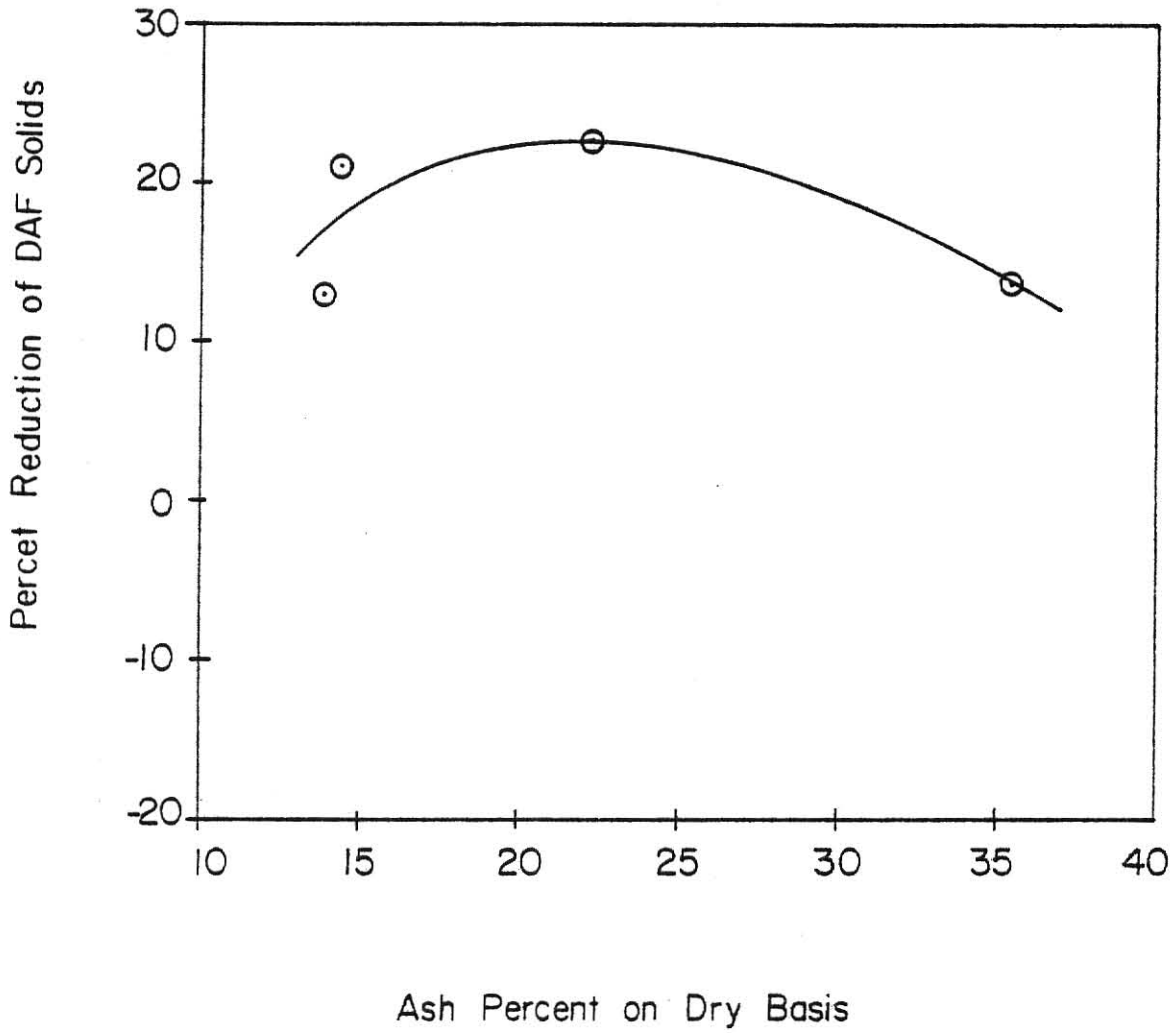


Figure 2. Effect of ash content on percent reduction of DAF solids:

Temperature = 380 °C (653 K)
Time = 60 minutes
Solvent-to-Coal ratio = 2:1.

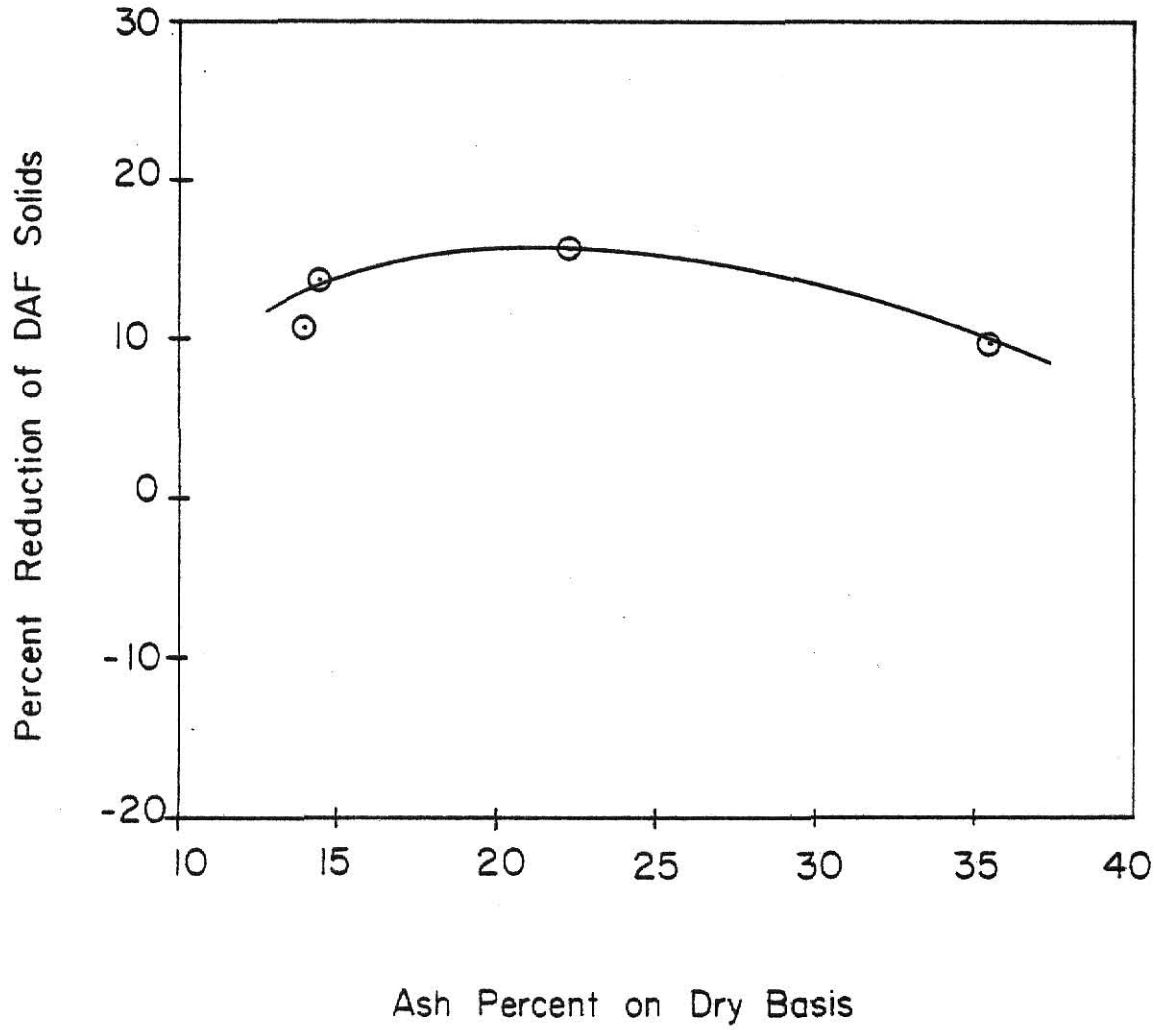


Figure 3. Effect of ash content on percent reduction of DAF solids:

Temperature = 400 °C (673 K)
Time = 30 minutes
Solvent-to-Coal ratio = 1:1.

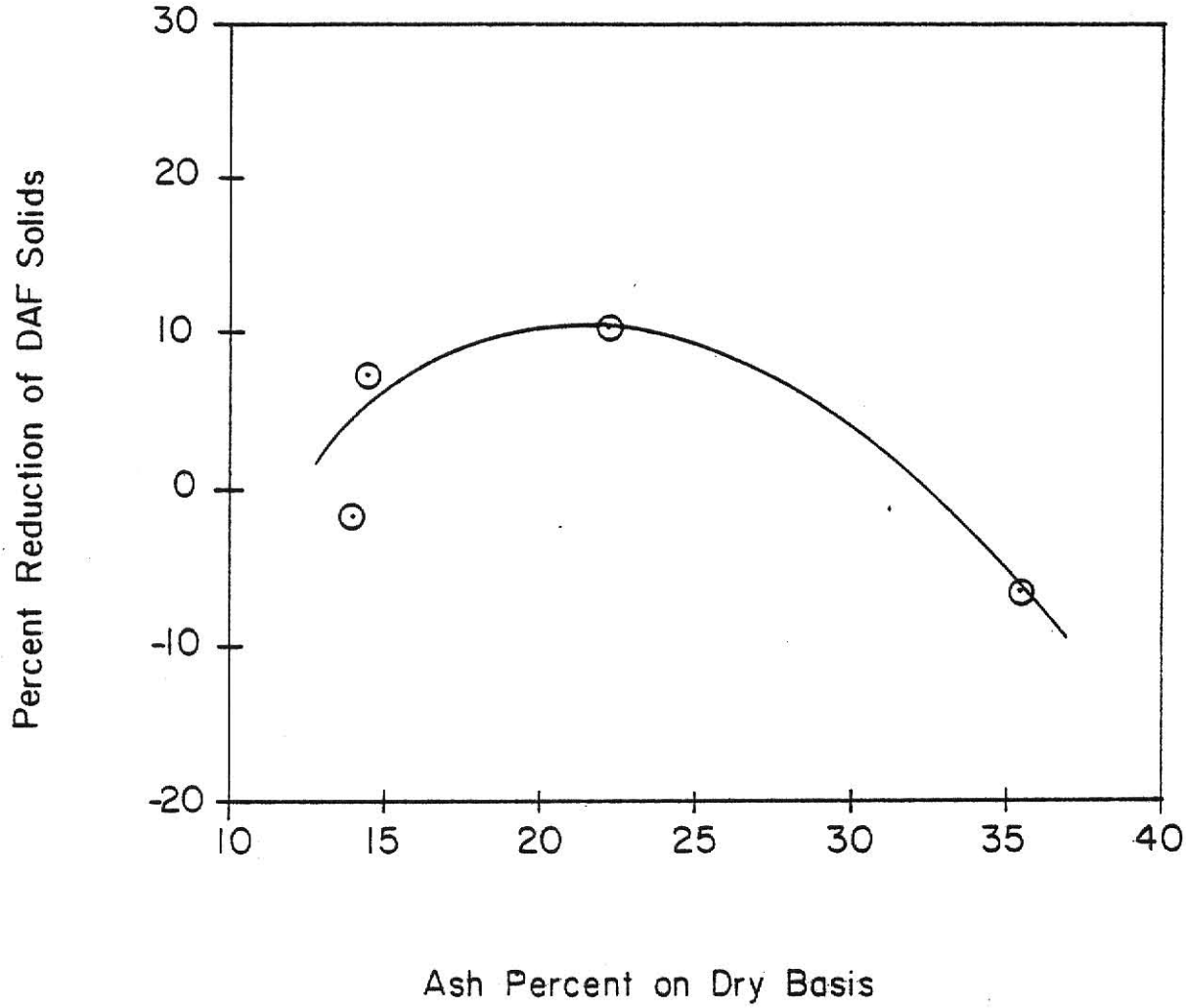


Figure 4. Effect of ash content on percent reduction of DAF solids:

Temperature = 420 °C (693 K)
Time = 30 minutes
Solvent-to-Coal ratio = 1.5:1.

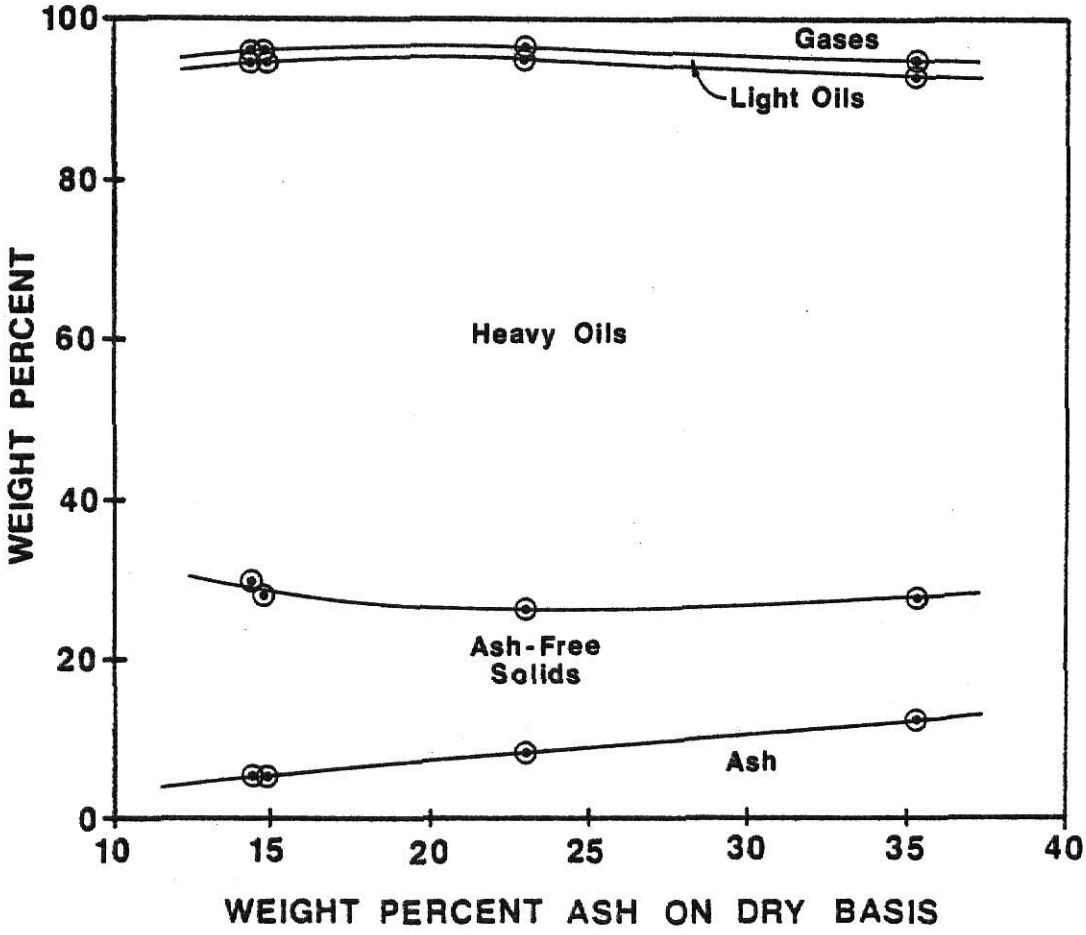


Figure 5. Effect of ash content on product distribution:

Temperature = 380 °C (653 K)
Time = 60 minutes
Solvent-to-Coal ratio = 2:1.

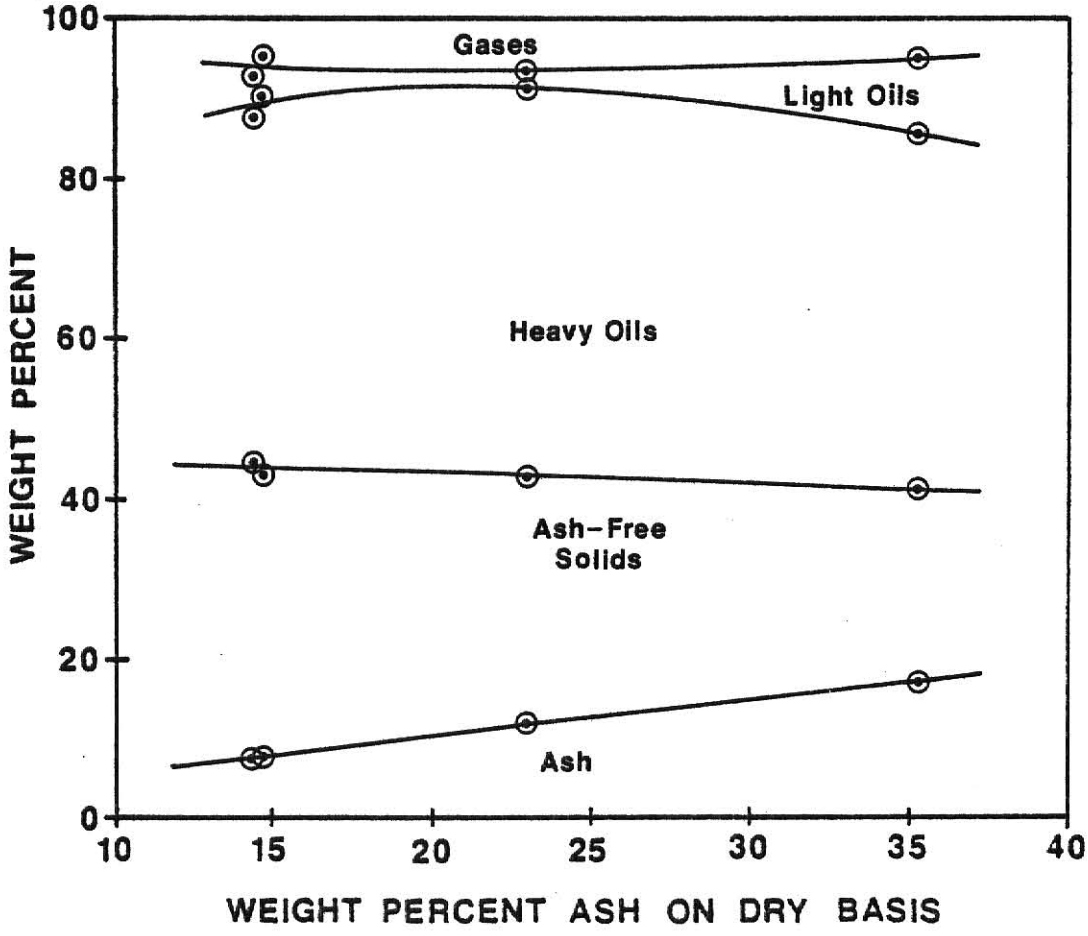


Figure 6. Effect of ash content on product distribution:

Temperature = 400 °C (673 K)
Time = 30 minutes
Solvent-to-Coal ratio = 1:1.

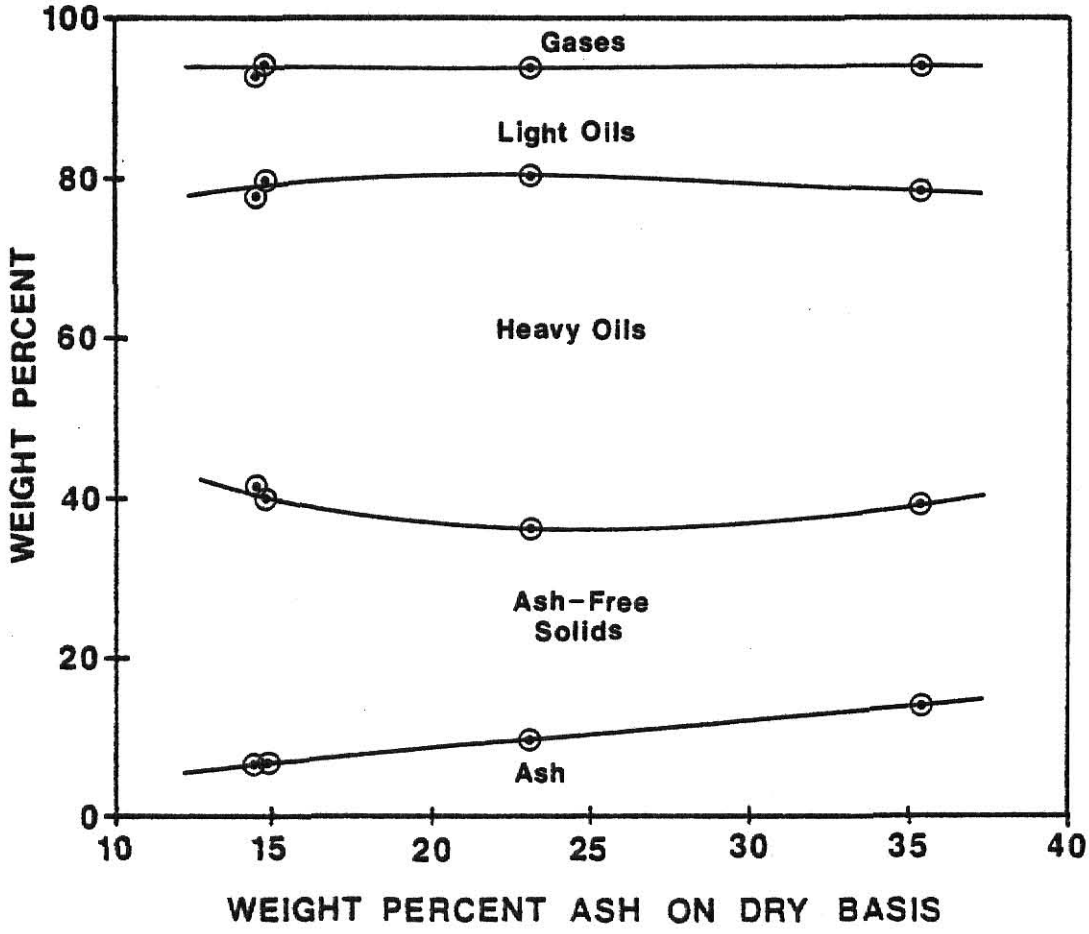


Figure 7. Effect of ash content on product distribution:

Temperature = 420 °C (693 K)
Time = 30 minutes
Solvent-to-Coal ratio = 1.5:1.

Table 1. Rowe Coal

| Component | As Received Basis Wt. % | Dry Basis Wt. % | Dry Ash-Free Basis Wt. % | Moisture Included as H & O Wt. % |
|---|---|---|---|---|
| Moisture | 1.64 | ——— | ——— | ——— |
| Carbon | 68.23 | 4.72 | 80.80 | 68.23 |
| Hydrogen | 4.64 | 4.72 | 5.50 | 4.82 |
| Nitrogen | 1.18 | 1.20 | 1.40 | 1.18 |
| Sulfur | 6.42 | 6.52 | 7.60 | 6.42 |
| Oxygen | 3.97 | 4.03 | 4.70 | 5.43 |
| Ash | 13.92 | 14.15 | ——— | 13.92 |
| | 100.00 | 99.99 | 100.00 | 100.00 |
| Elemental Ratios Dry Basis | H/C = 0.711 | | O/H = 0.054 | |

Table 2. Bevier Coal

| Component | As Received Basis Wt. % | Dry Basis Wt. % | Dry Ash-Free Basis Wt. % | Moisture Included as H & O Wt. % |
|---|---|---|---|---|
| Moisture | 2.70 | ——— | ——— | ——— |
| Carbon | 65.09 | 66.90 | 78.18 | 65.09 |
| Hydrogen | 4.51 | 4.64 | 5.42 | 4.81 |
| Nitrogen | 1.08 | 1.11 | 1.30 | 1.08 |
| Sulfur | 5.11 | 5.25 | 6.14 | 5.11 |
| Oxygen | 7.46 | 7.67 | 8.96 | 9.86 |
| Ash | 14.04 | 14.43 | ——— | 14.04 |
| | 99.99 | 100.00 | 100.00 | 100.00 |

Elemental Ratios Dry Basis: H/C = 0.826 O/H = 0.104

Table 3. Baxter Coal

| Component | As Received Basis Wt. % | Dry Basis Wt. % | Dry Ash-Free Basis Wt. % | Moisture Included as H & O Wt. % |
|---|---|---|---|---|
| Moisture | 2.59 | ——— | ——— | ——— |
| Carbon | 61.24 | 62.87 | 81.53 | 62.24 |
| Hydrogen | 4.22 | 4.33 | 5.62 | 4.51 |
| Nitrogen | 1.07 | 1.09 | 1.42 | 1.07 |
| Sulfur | 4.56 | 4.68 | 6.07 | 4.56 |
| Oxygen | 4.02 | 4.13 | 5.35 | 6.32 |
| Ash | 22.30 | 22.89 | ——— | 22.30 |
| | 100.00 | 99.99 | 99.99 | 100.00 |
| Elemental Ratios Dry Basis | H/C = 0.821 | | O/H = 0.060 | |

Table 4. Mulberry Coal

| Component | As Received Basis Wt. % | Dry Basis Wt. % | Dry Ash-Free Basis Wt. % | Moisture Included as H & O Wt. % |
|---|---|---|---|---|
| Moisture | 8.22 | ——— | ——— | ——— |
| Carbon | 47.01 | 51.22 | 79.51 | 47.01 |
| Hydrogen | 2.90 | 3.16 | 4.91 | 3.81 |
| Nitrogen | 0.88 | 0.95 | 1.48 | 0.88 |
| Sulfur | 3.55 | 3.87 | 6.00 | 3.55 |
| Oxygen | 4.79 | 5.22 | 8.10 | 12.10 |
| Ash | 32.65 | 35.57 | ——— | ——— |
| | 100.00 | 99.99 | 100.00 | 100.00 |
| Elemental Ratios Dry Basis | H/C = 0.736 | | O/H = 0.104 | |

# CHAPTER V

# RECOMMENDATIONS FOR FUTURE WORK

# CONCLUDING REMARKS

The current energy situation in the United States is forcing major consumers of petroleum and natural gas to consider conversion to a coal-based fuel. If the Kyushu-Koshi solvolysis process could be made more efficient in its use of hydrogen a greater proportion of the coal could be converted to a heavy fuel oil. The experimental results of this work on Rowe, Bevier, Baxter, and Mulberry coals suggest that conversion to benzene soluble products in the Kyushu-Koshi process is no more favorable for Kansas bituminous coals than for other coals reported in the literature. Extremely favorable reported conversions using the Kyushu-Koshi atmospheric process must be studied in light of the separation solvent effect observed in Chapter III. Comparison of different coal conversions must be based on the same separation solvent and attribute the proper amount of conversion to the solvent and the liquefaction process.

Coking of asphaltenes to benzene insoluble solids appears to be the major drawback in the Kyushu-Koshi process. Currently the process is carried out in such a manner so that hydrogen-rich gases and light oils are allowed to boil off from the reaction slurry at about 400 $^{o}$C (673 K). As these streams leave the reaction vessel the total hydrogen available for transfer to the thermally induced coal free radical fragments decreases to the point where asphaltenes present originally as the solvolysis agent are dehydrogenated to form benzene insolubles. This dehydrogenation is apparently promoted catalytically by minerals present in the coal ash.

Further study of the Kyushu-Koshi process should concentrate on reversing excessive dehydrogenation of the process solvent. Continued

contact of gases and light oils with the reaction slurry either by reflux of a totally enclosed batch system, operation at pressures above one atmosphere, and/or operation of the reaction slurry under a hydrogen gas blanket would all increase the hydrogen partial pressure above the slurry, increasing conversion.

Additional investigation of the effect of coal ash content should be conducted in a manner such that the variation of solvent to organic coal matter with different ash contents would be eliminated. By altering the amount of solvent charged with the different ash content the true effect of ash content on the solvolysis reaction would become easier to discern.

It is also desirable to measure the volume of product gas evolved during liquefaction. This information will be needed to complete the material balance for the process.

Further refinement of the Kyushu-Koshi solvolysis process may provide an additional option in the search for coal conversion schemes.

# APPENDIX 1

## EXPERIMENTAL RESULTS:

## SOLVOLYSIS LIQUEFACTION OF A KANSAS COAL

This appendix contains the experimental results of the study presented in Chapter III. Figures 1-12 present the effect of reaction time on the percent reduction of DAF solids and product distribution. The effect of reaction temperature is shown in Figures 13-26. The effect of coal on product distribution is given in Figure 27. Figures 28-42 present the effect of the solvent-to-coal weight ratio on solids reduction and product distribution. The proportional amounts of gases and light oils produced in the solvolysis reaction are shown in Figures 43-48, based on the amounts of coal and/or asphalt charged. Figures 49 and 50 present the major components and the elemental composition of the gaseous product stream at three reaction conditions. For a complete explanation of the plots and terms used in this appendix consult Chapter III.

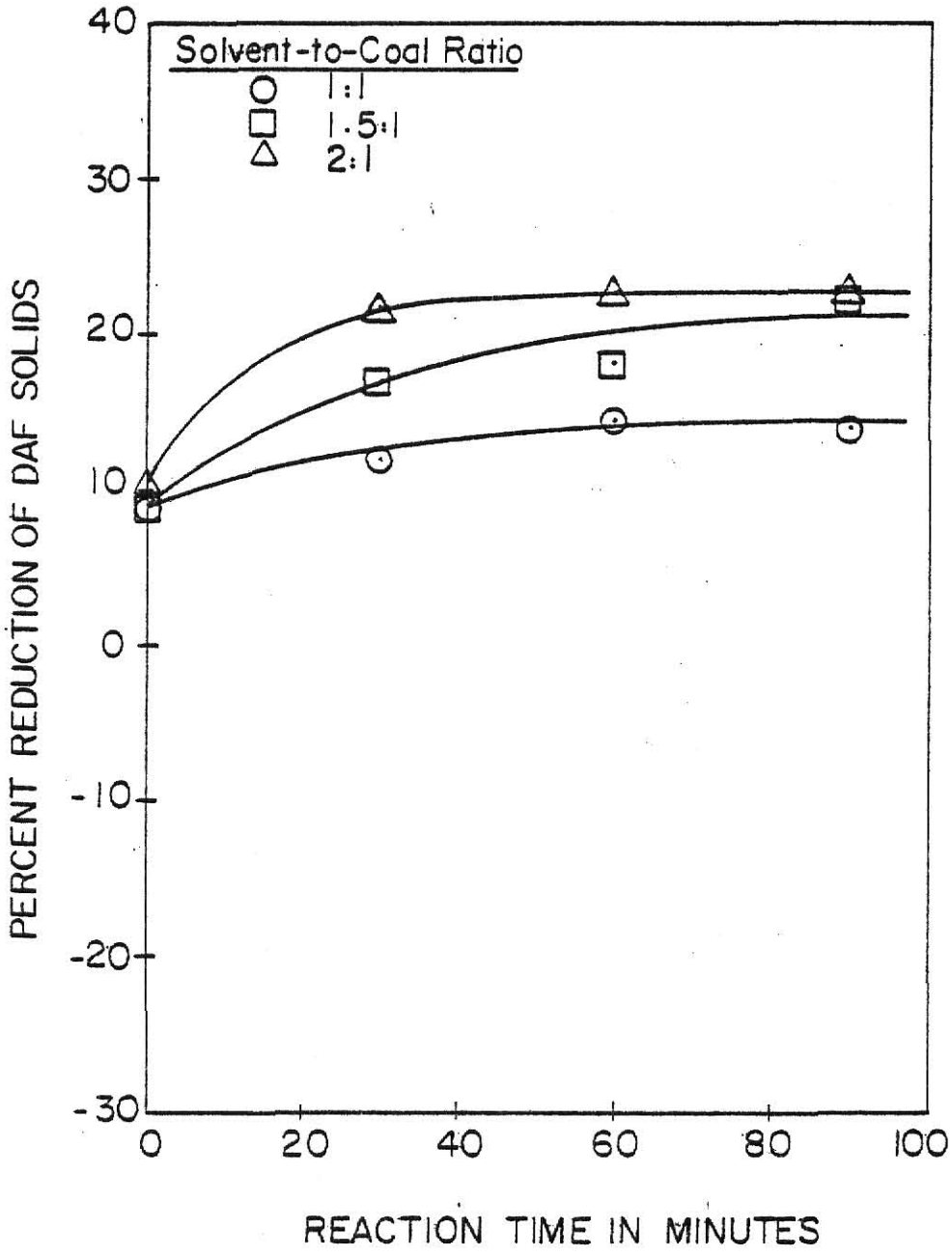


Figure 1. Effect of reaction time on solids reduction:

Temperature = 380 °C (653 K).

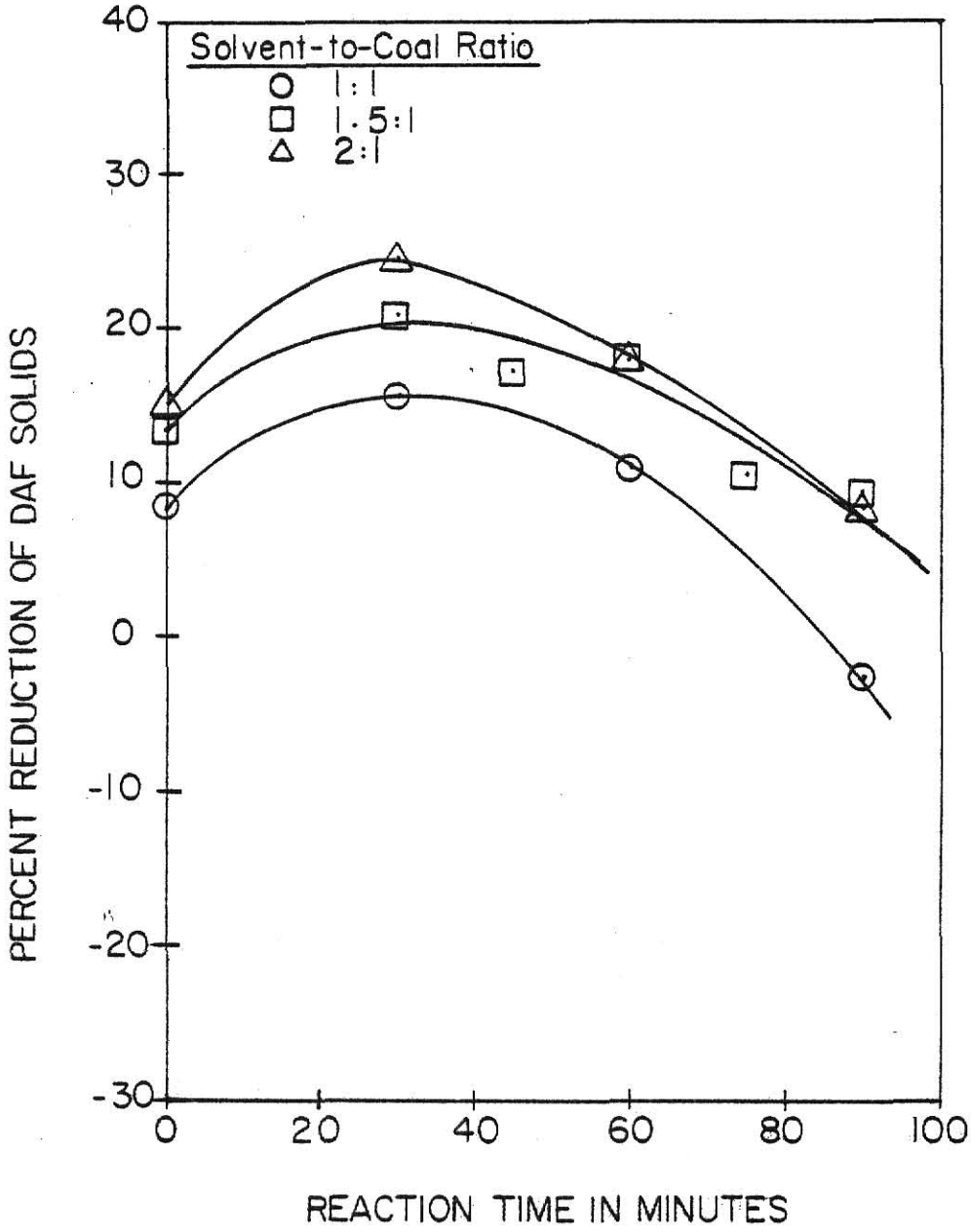


Figure 2. Effect of reaction time on solids reduction:

Temperature = 400 $^{o}$C (673 K).

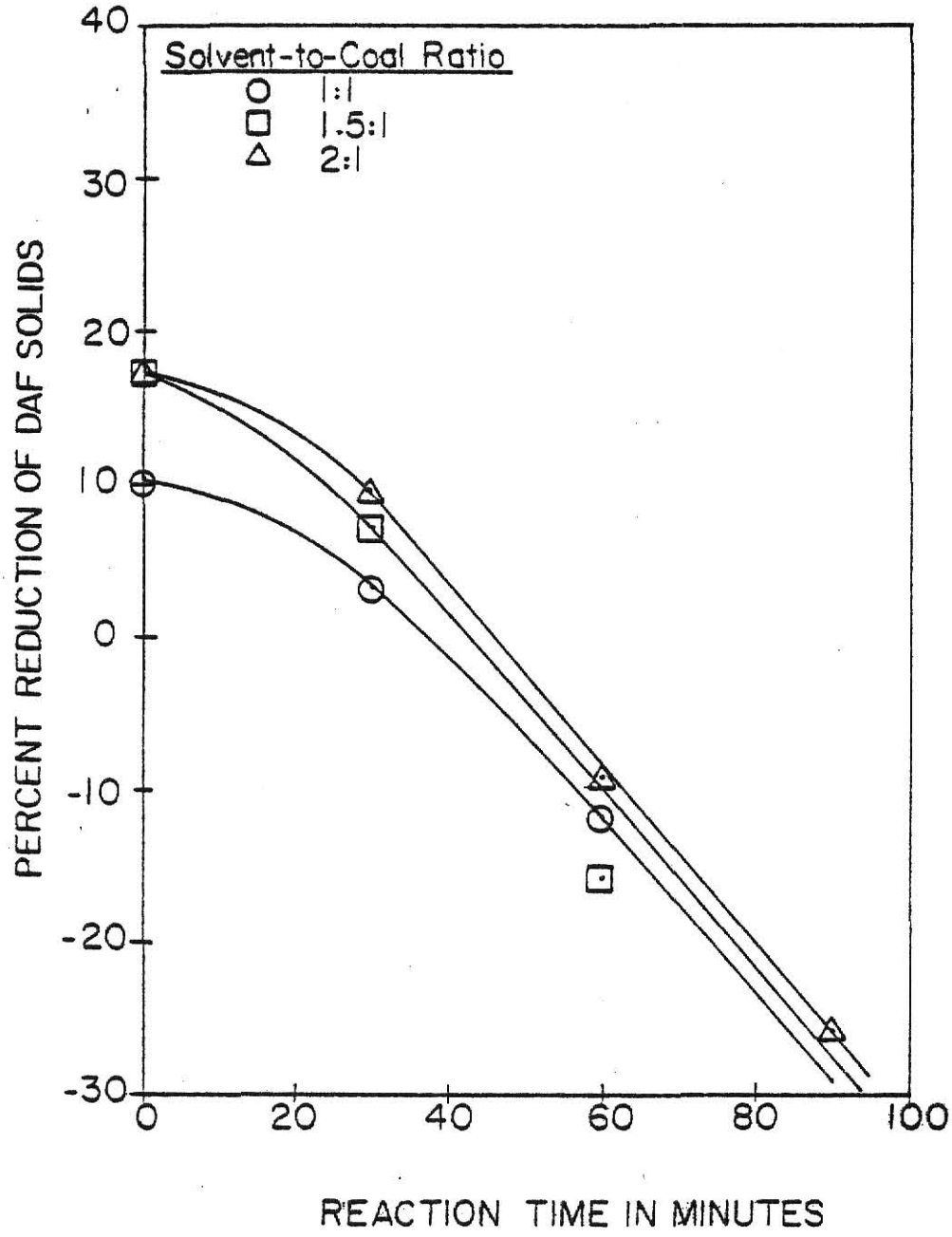


Figure 3. Effect of reaction time on solids reduction:

Temperature = 420 °C (693 K).

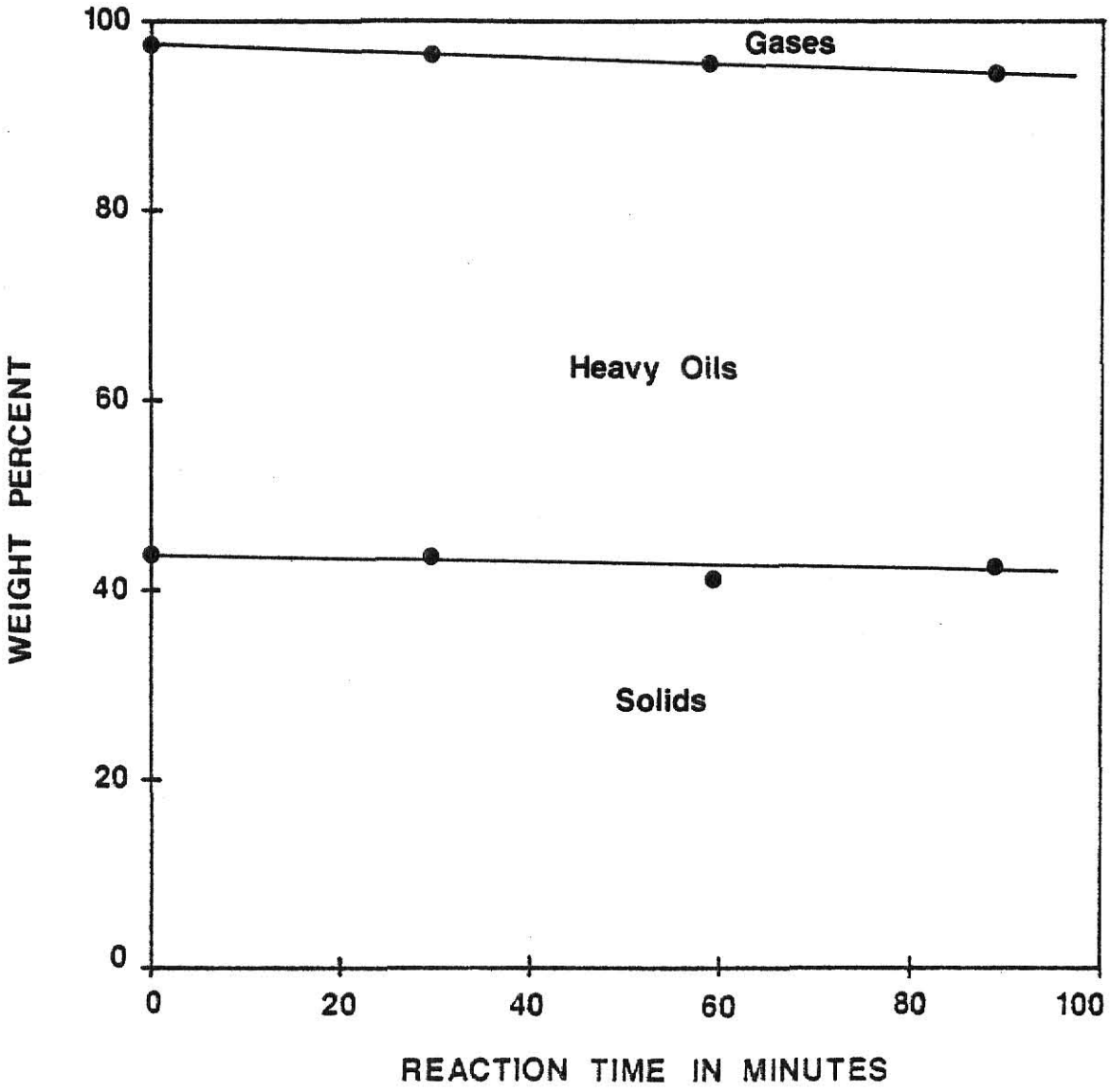


Figure 4. Effect of reaction time on product distribution:

Temperature = 380 $^{o}$C (653 K)
Solvent-to-Coal ratio = 1:1

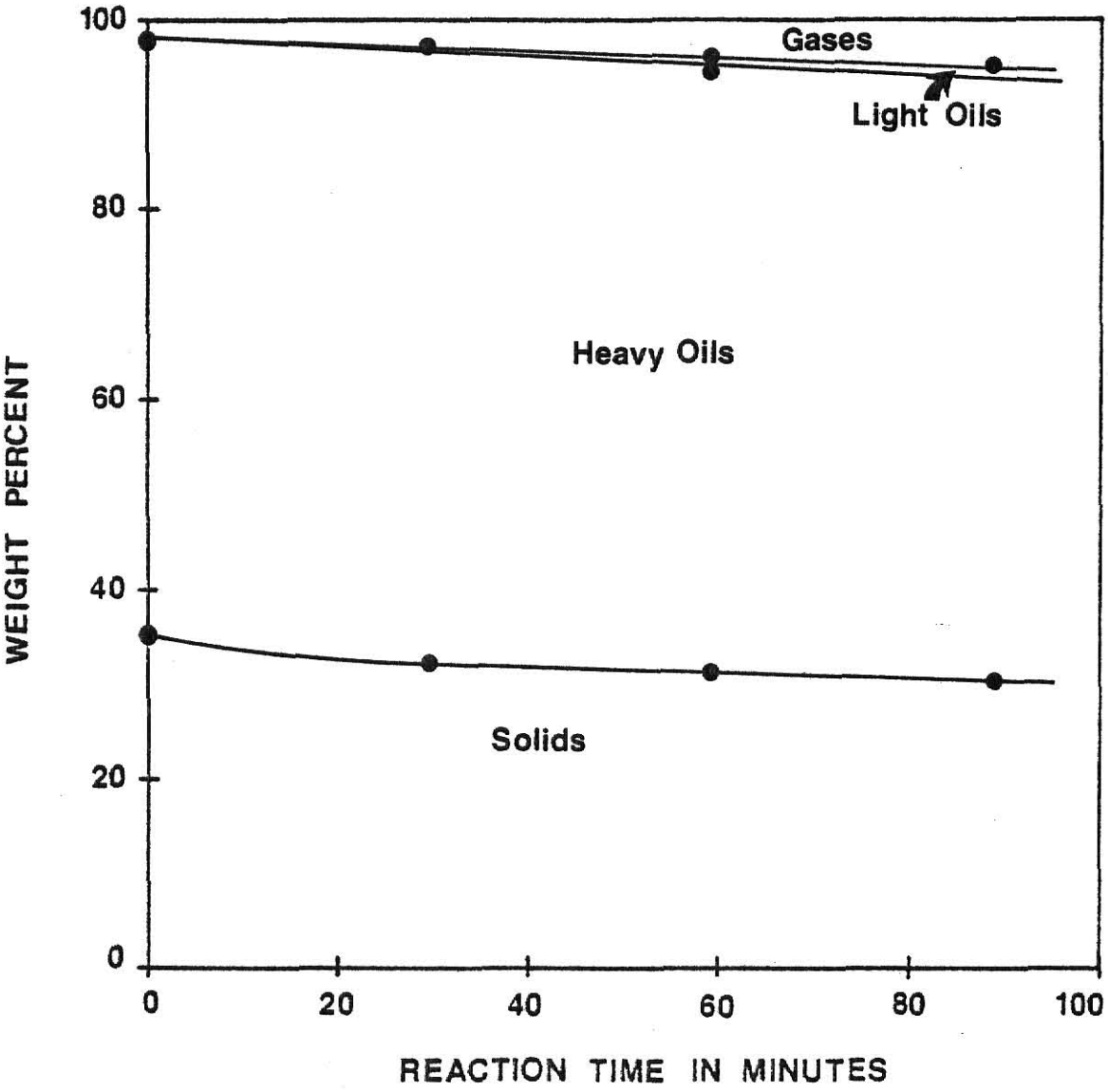


Figure 5. Effect of reaction time on product distribution:

Temperature = 380 °C (653 K)
Solvent-to-Coal ratio = 1.5:1.

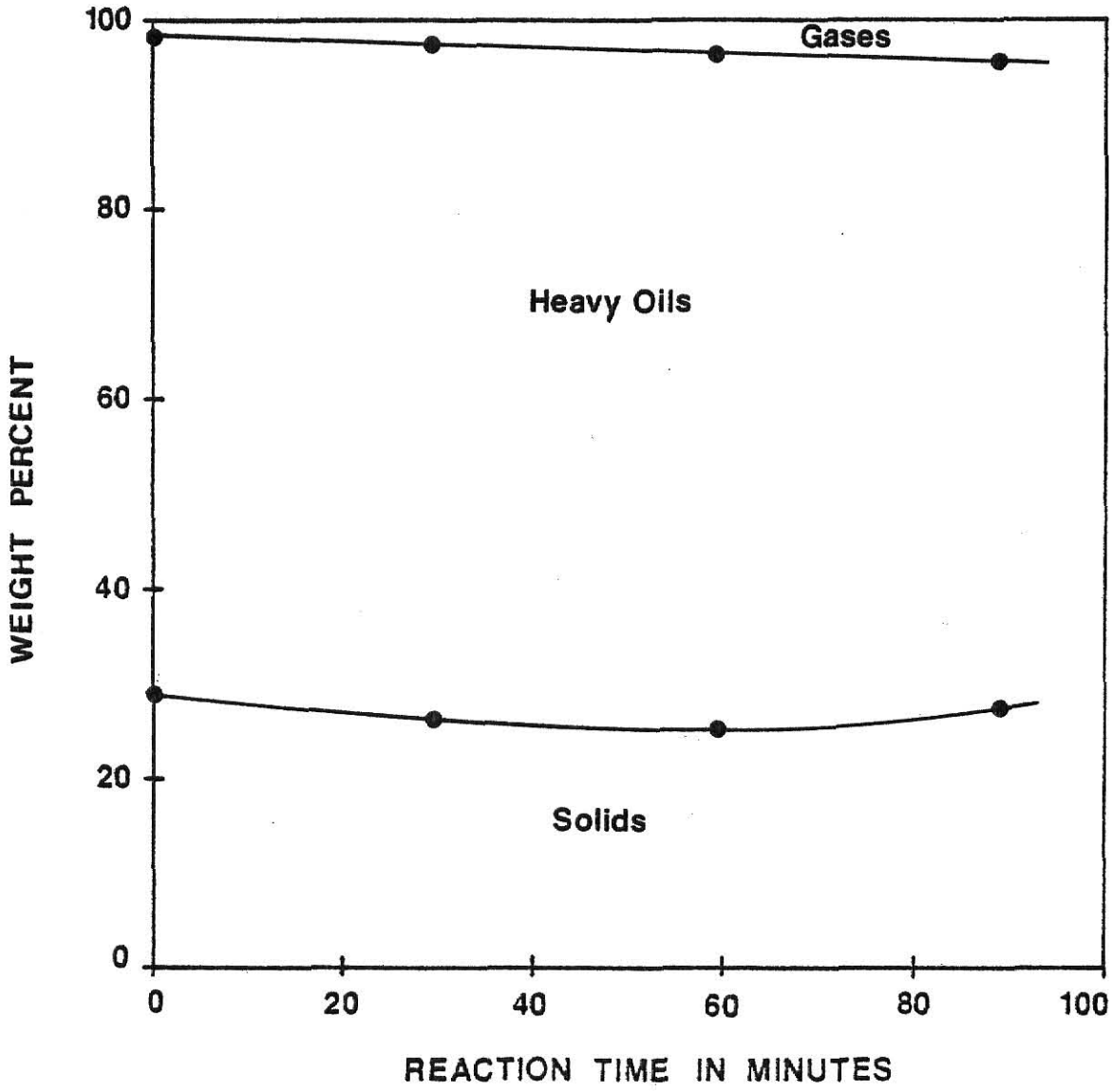


Figure 6. Effect of reaction time on product distribution:

Temperature = 380 °C (653 K)
Solvent-to-Coal ratio = 2:1.

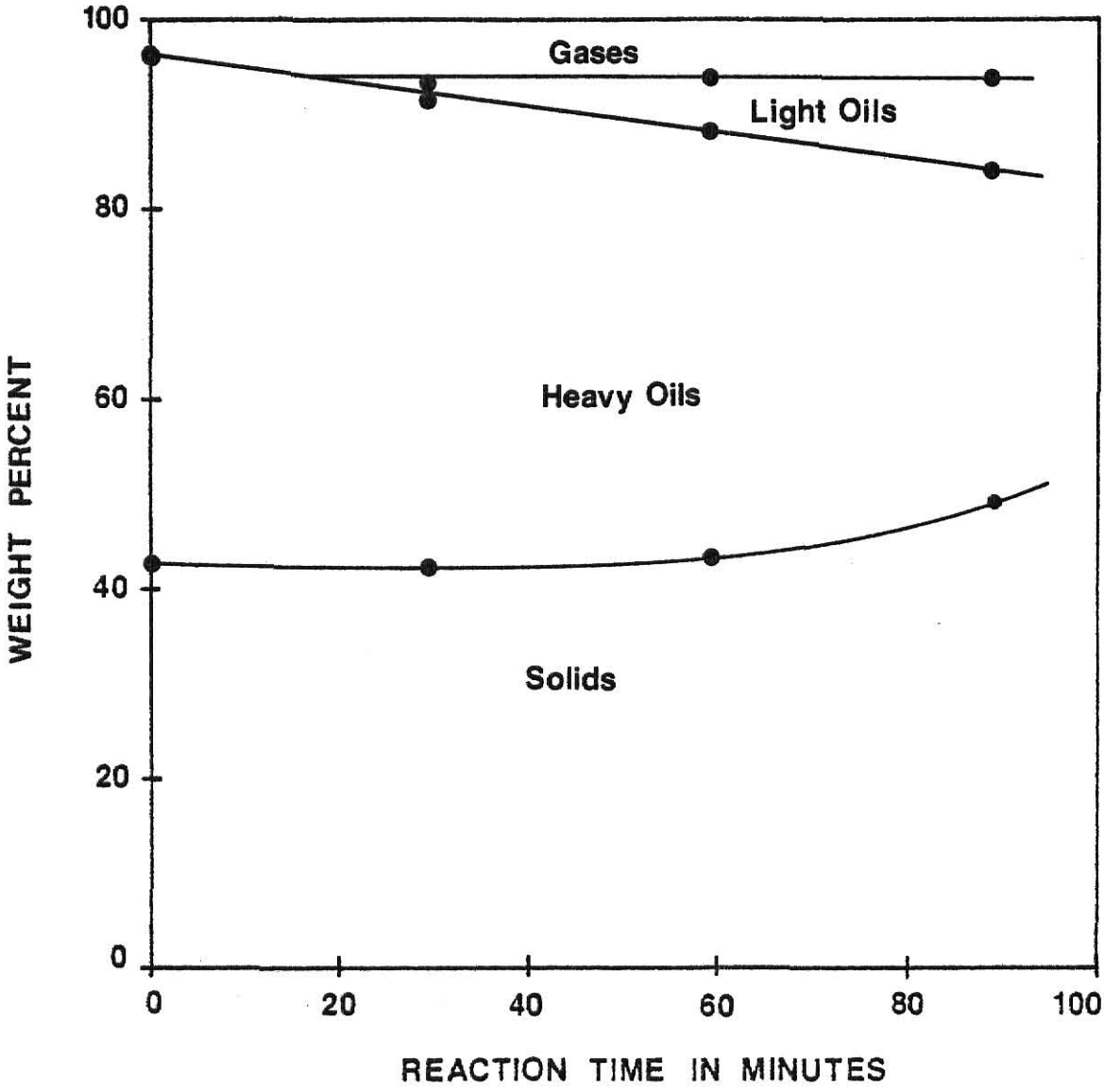


Figure 7. Effect of reaction time on product distribution:

Temperature = 400 °C (673 K)
Solvent-to-Coal ratio = 1:1.

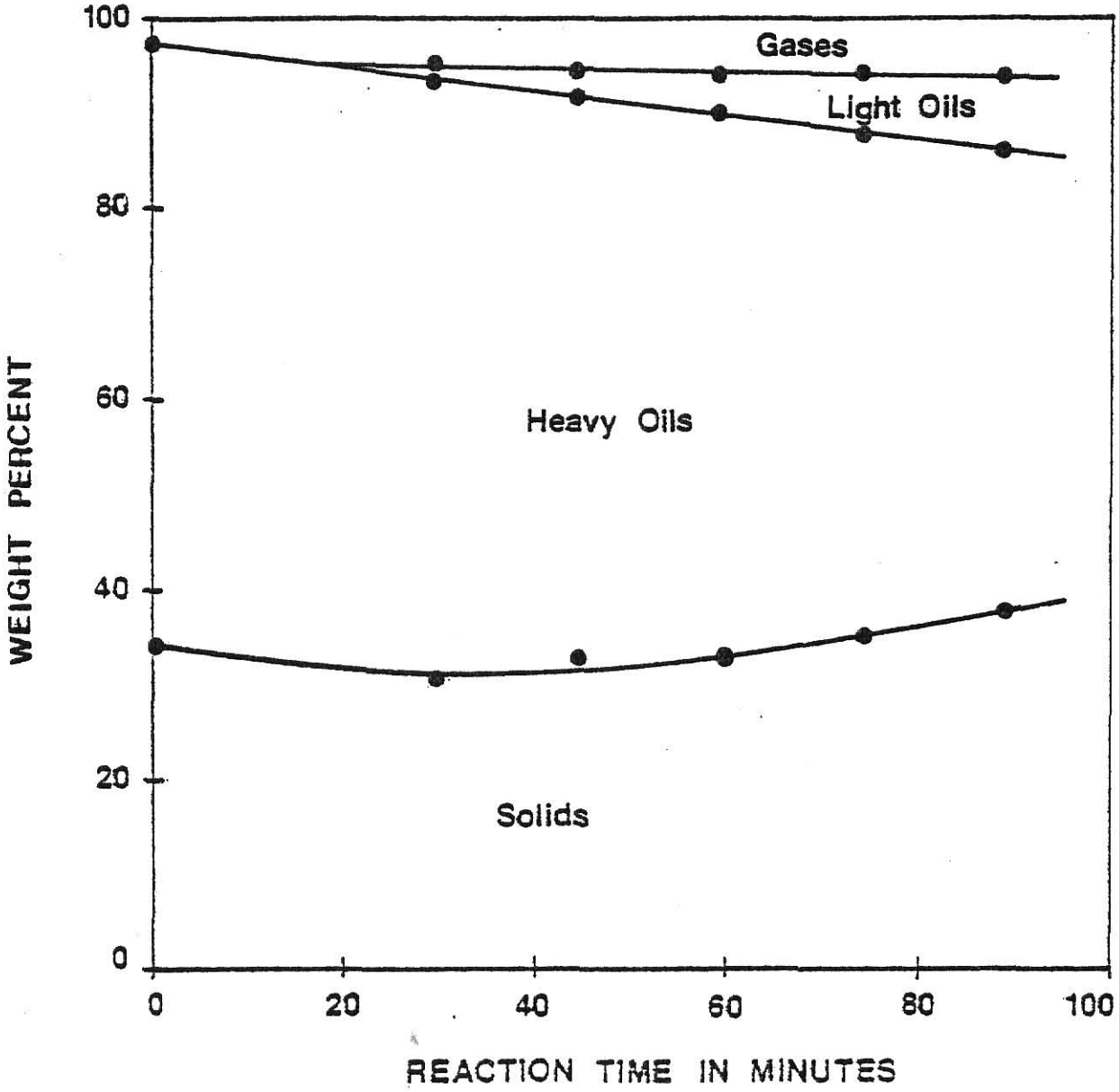


Figure 8. Effect of reaction time on product distribution:

Temperature = 400 $^{o}$C (673 K)
Solvent-to-Coal ratio = 1.5:1.

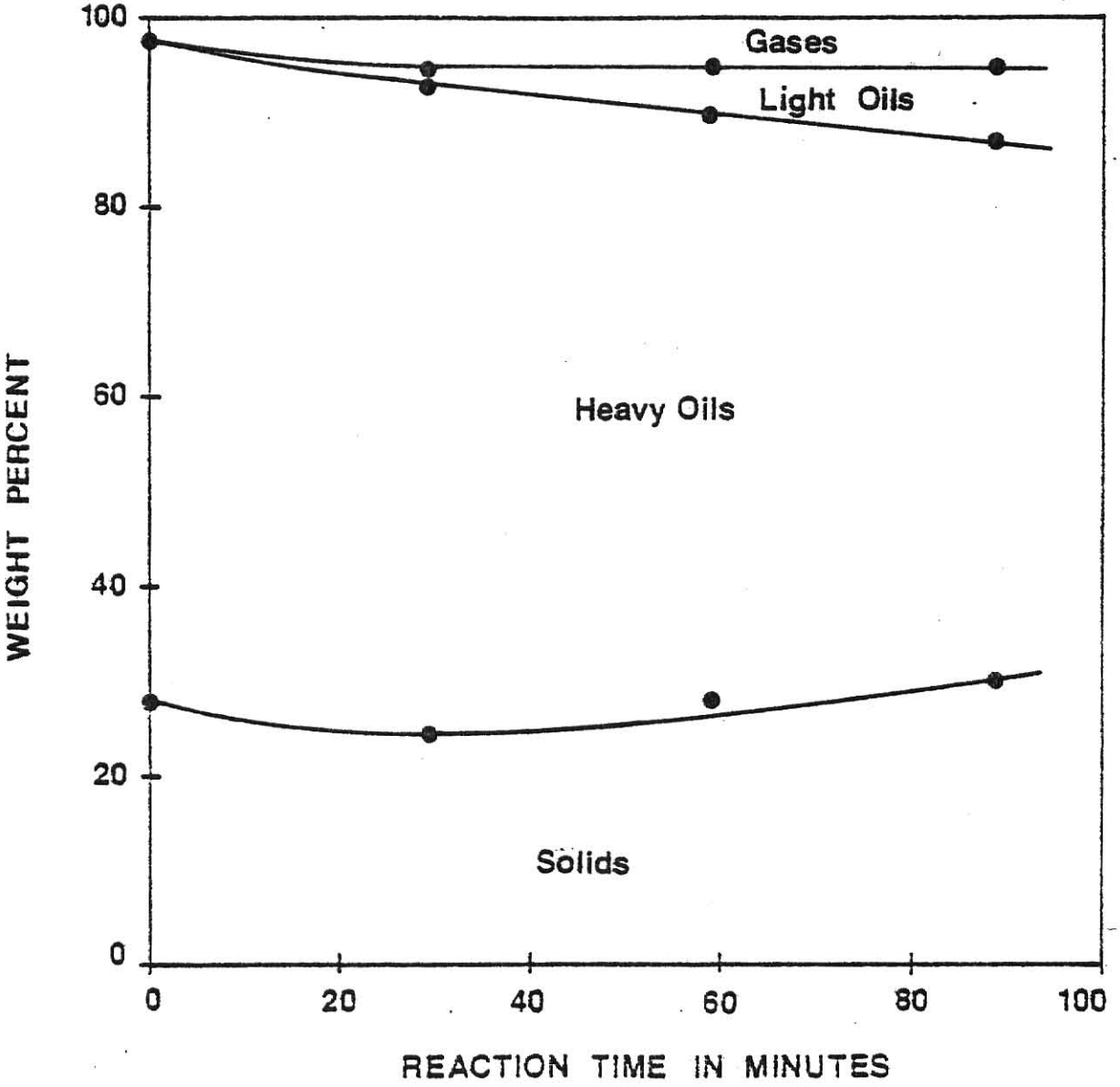


Figure 9. Effect of reaction time on product distribution:

Temperature = 400 $^{o}$C (673 K)
Solvent-to-Coal ratio = 2:1.

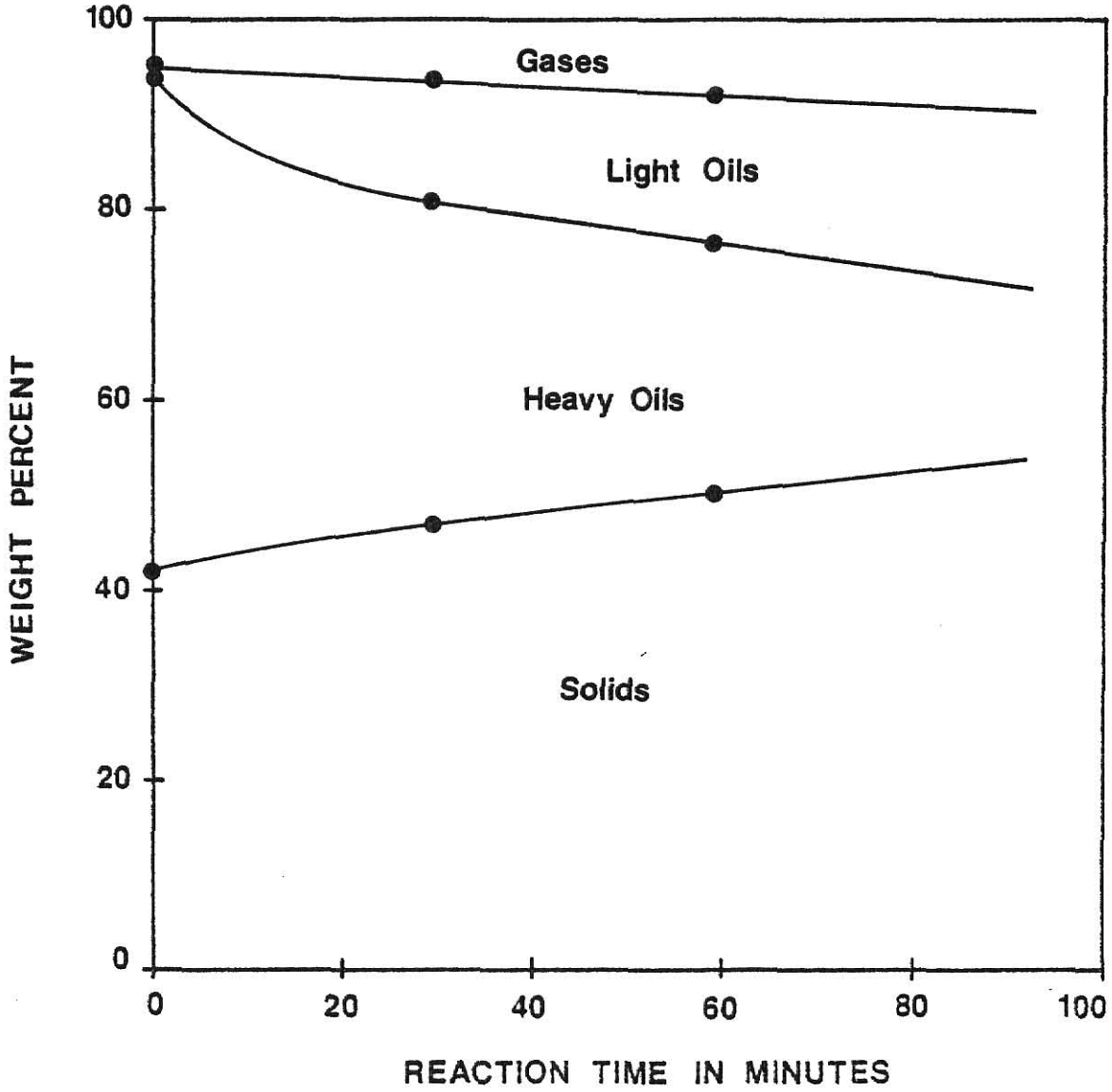


Figure 10. Effect of reaction time on product distribution:

Temperature = 420 $^{o}$C (693 K)
Solvent-to-Coal ratio = 1:1.

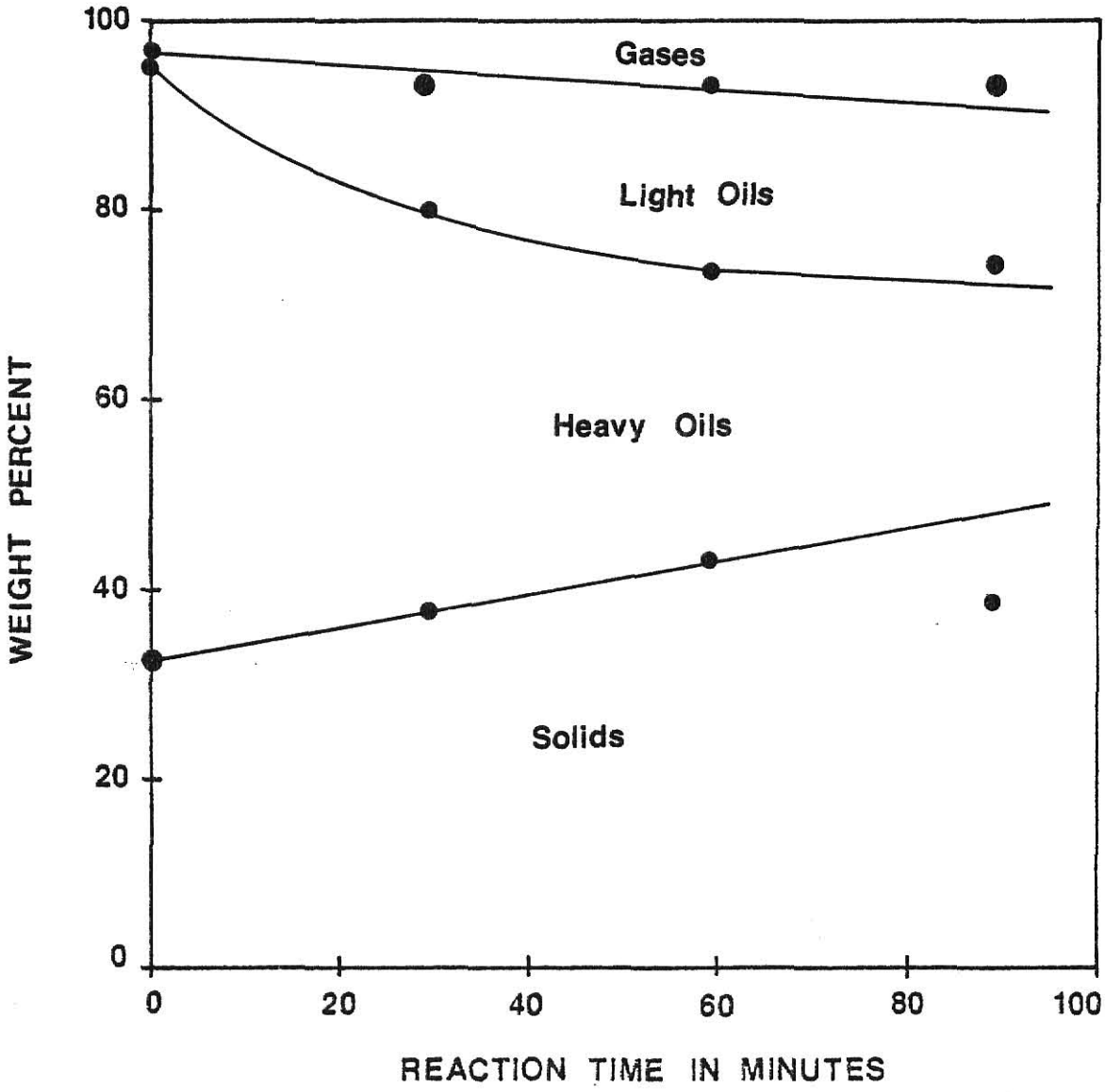


Figure 11. Effect of reaction time on product distribution:

Temperature = 420 $^{o}$C (693 K)
Solvent-to-Coal ratio = 1.5:1.

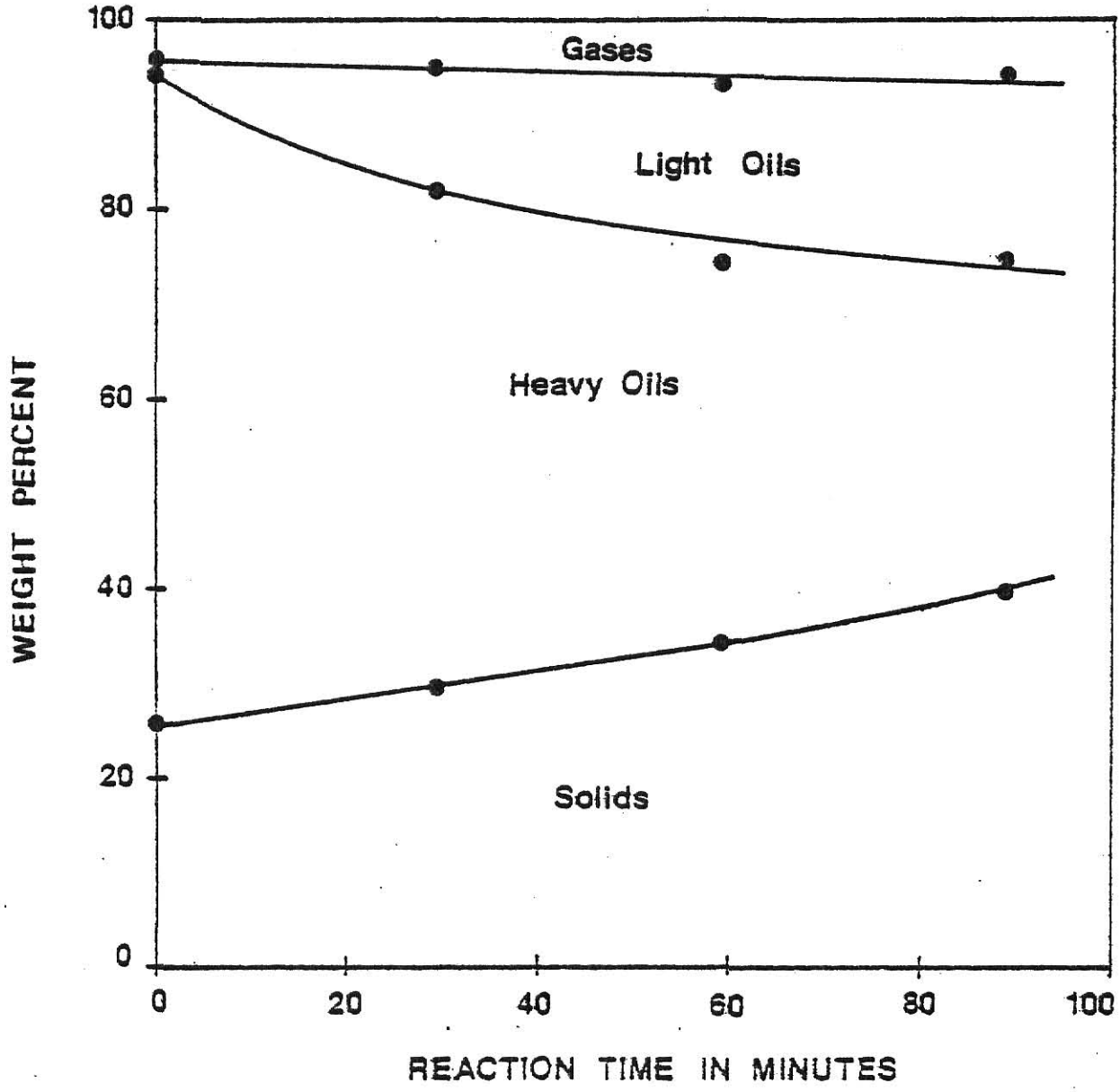


Figure 12. Effect of reaction time on product distribution:

Temperature = 420 $^{o}$C (693 K)
Solvent-to-Coal ratio = 2:1.

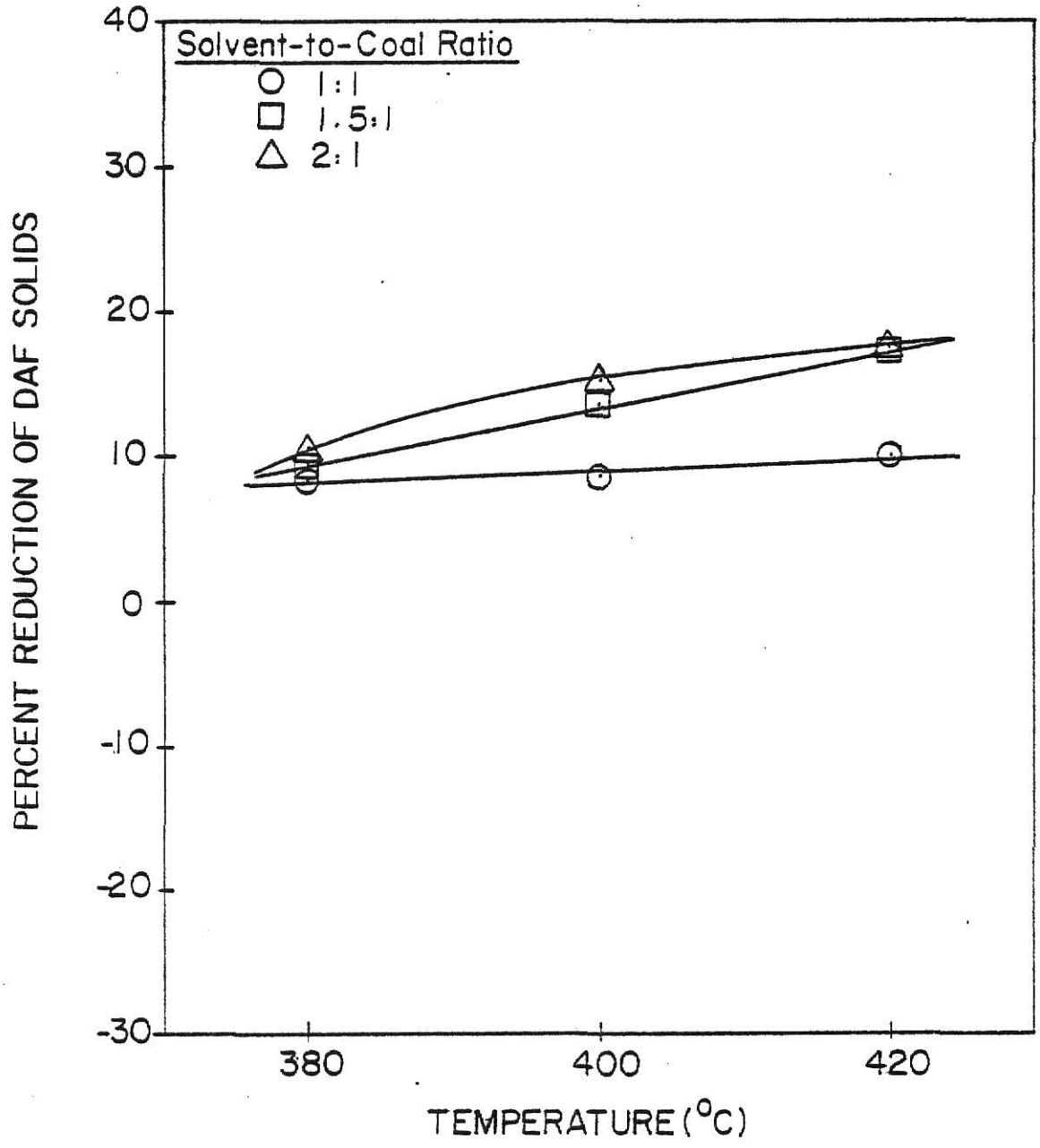


Figure 13. Effect of reaction temperature on solids reduction:

Time = 0 minutes.

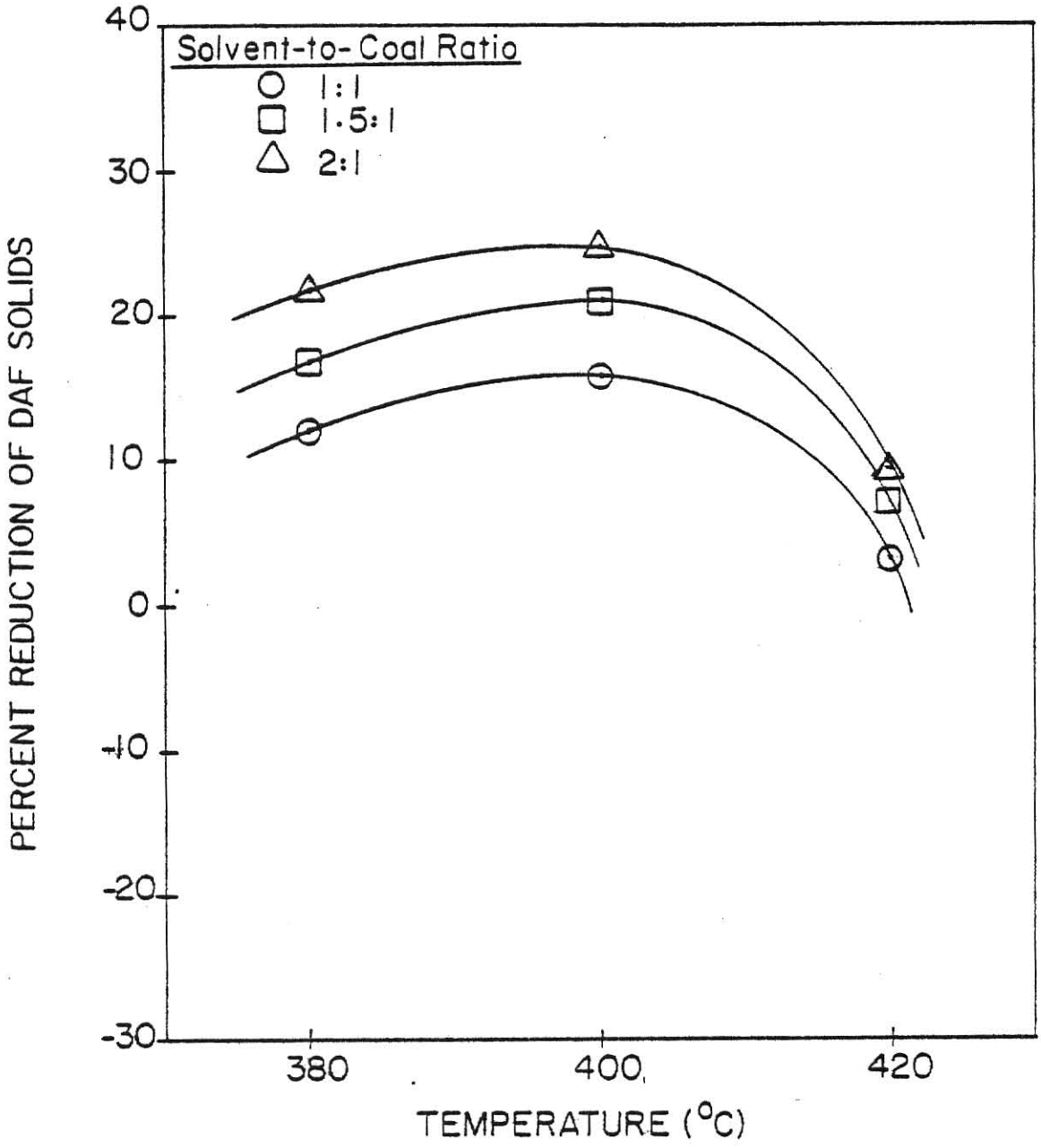


Figure 14. Effect of reaction temperature on solids reduction:

Time = 30 minutes.

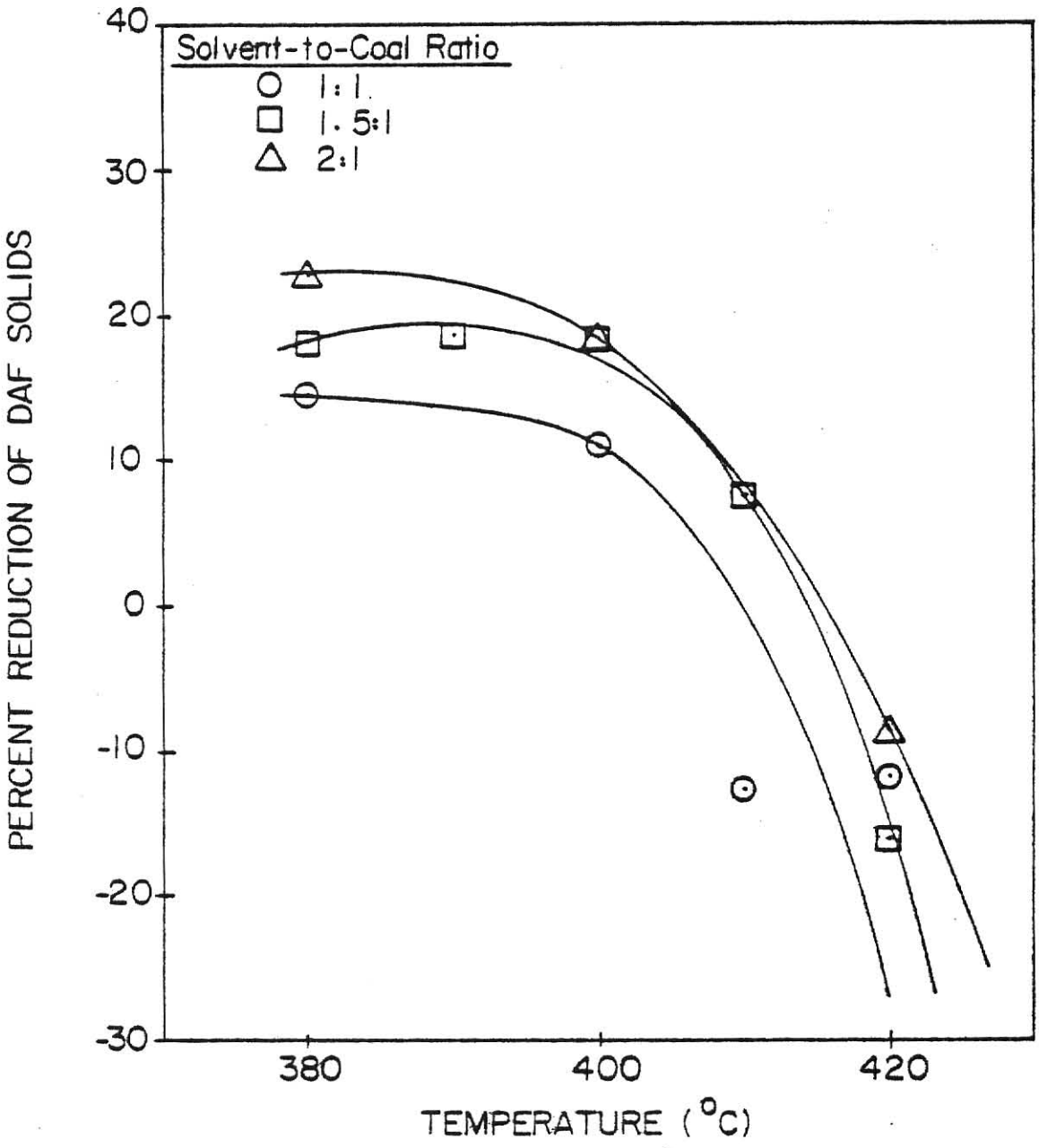


Figure 15. Effect of reaction temperature on solids reduction:

Time = 60 minutes.

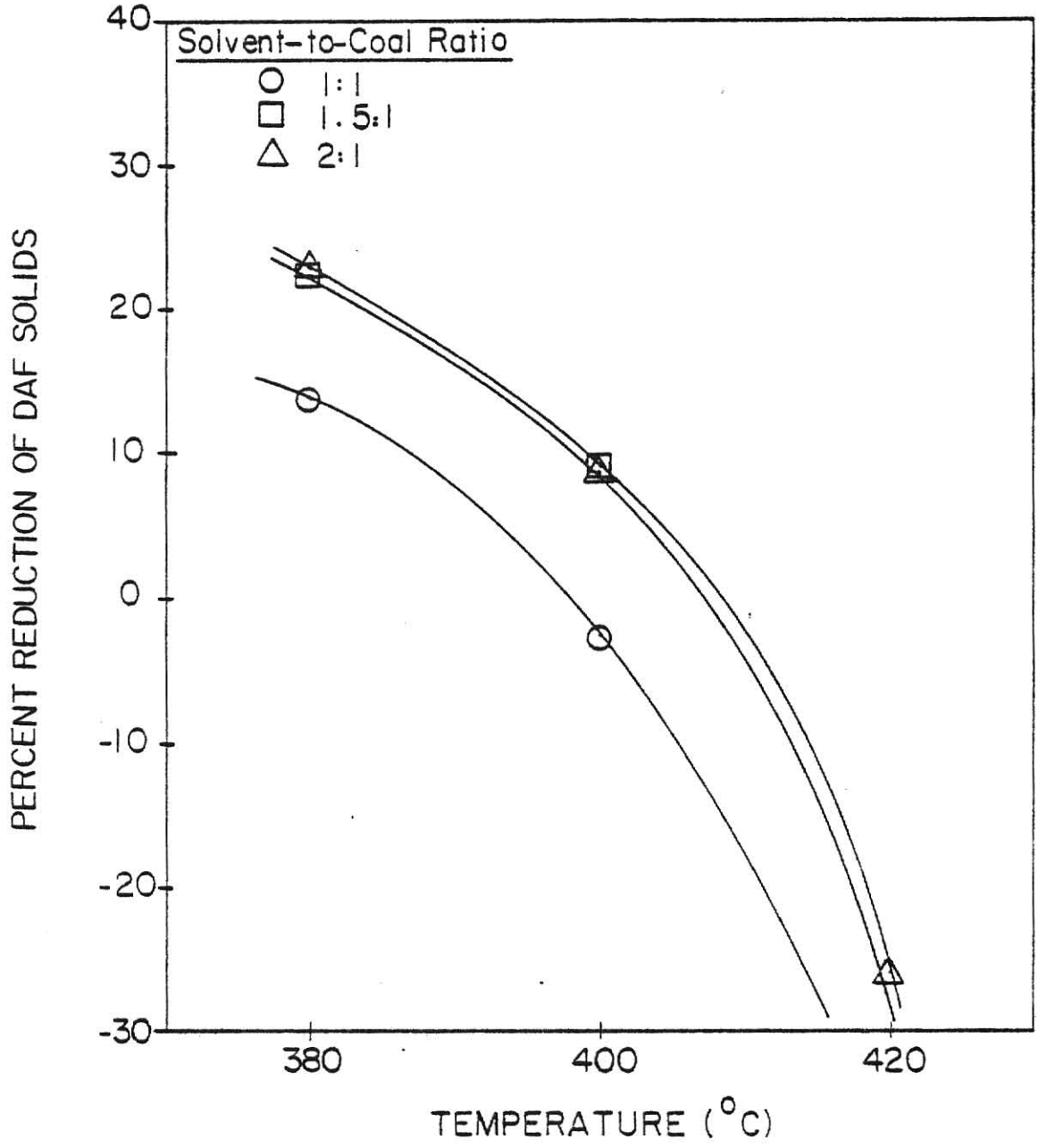


Figure 16. Effect of reaction temperature on solids reduction:

Time = 90 minutes.

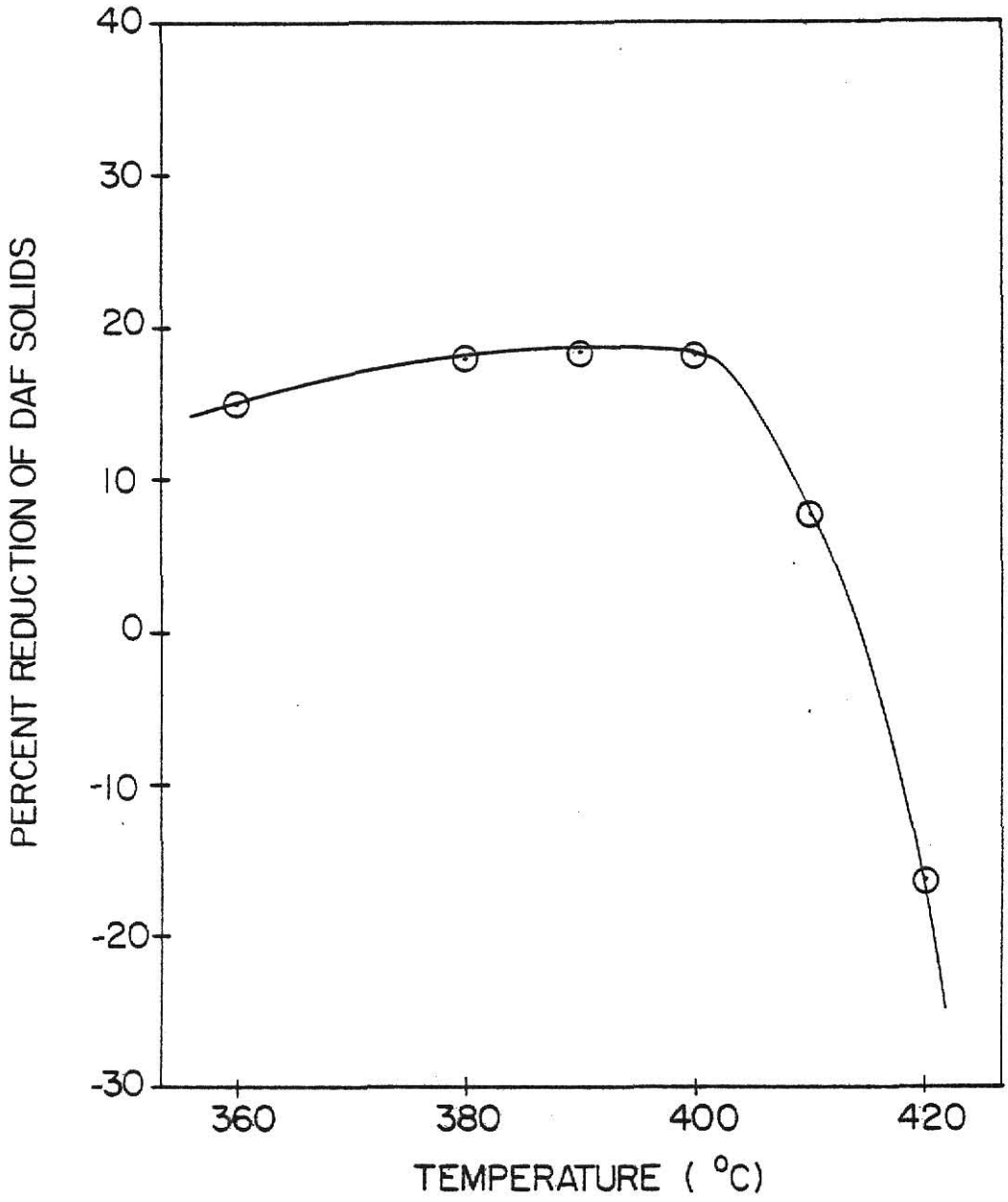


Figure 17. Effect of reaction temperature on solids reduction:

Time = 60 minutes
Solvent-to-Coal ratio = 1.5:1.

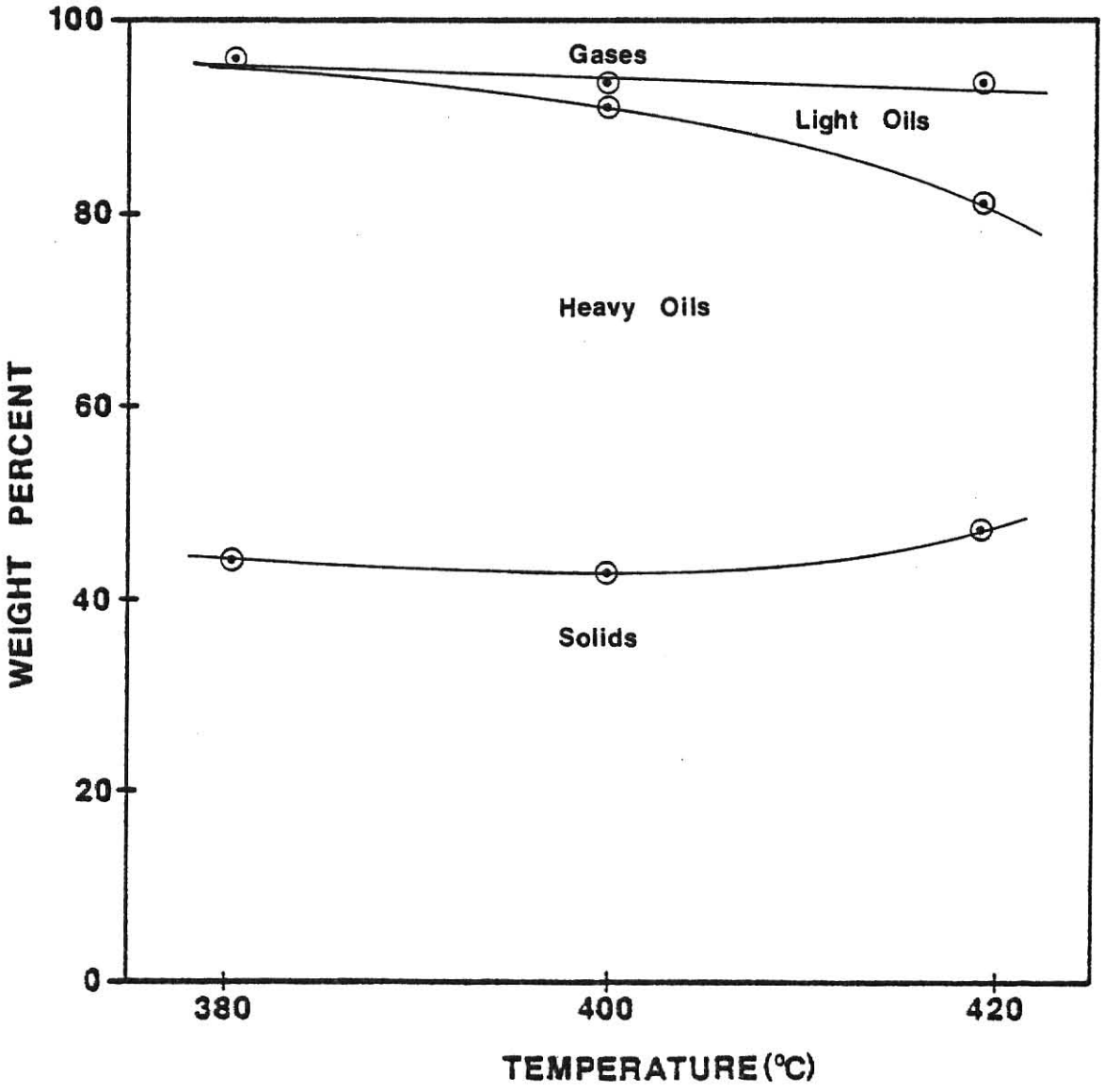


Figure 18. Effect of reaction temperature on product distribution:

Time = 30 minutes
Solvent-to-Coal ratio = 1:1.

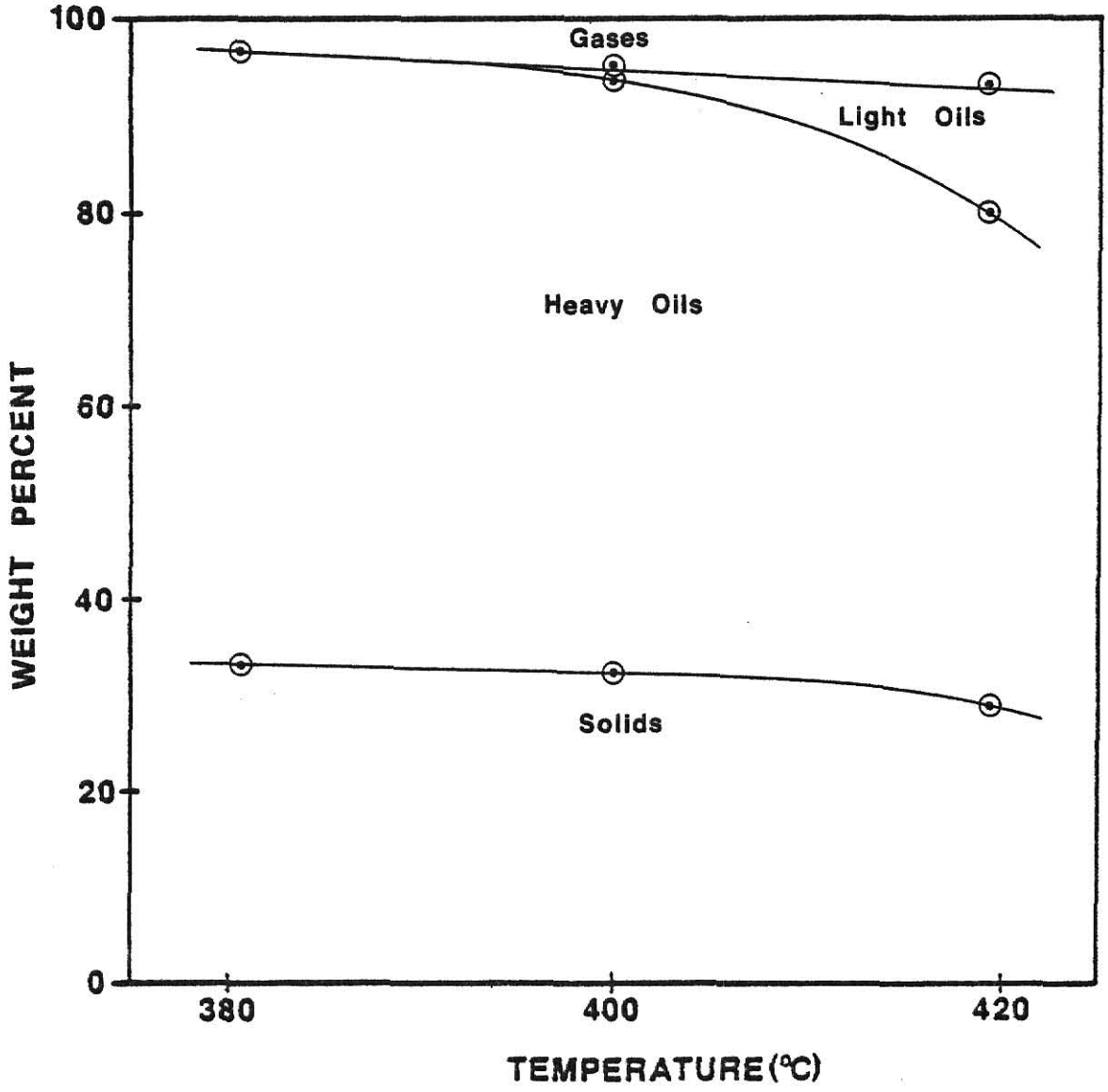


Figure 19. Effect of reaction temperature on product distribution:

Time = 30 minutes
Solvent-to-Coal ratio = 1.5:1.

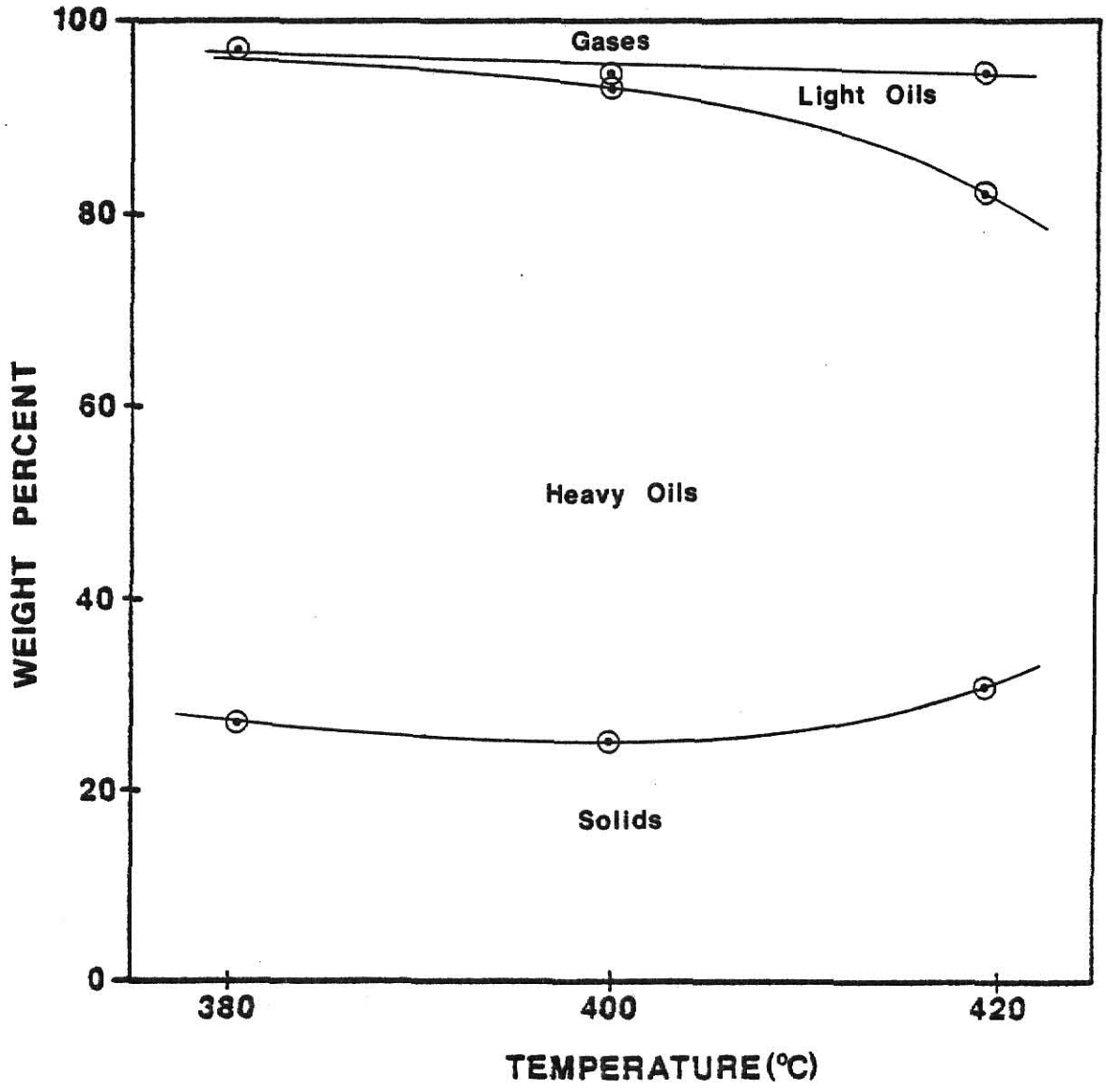


Figure 20. Effect of reaction temperature on product distribution:

Time = 30 minutes
Solvent-to-Coal ratio = 2:1.

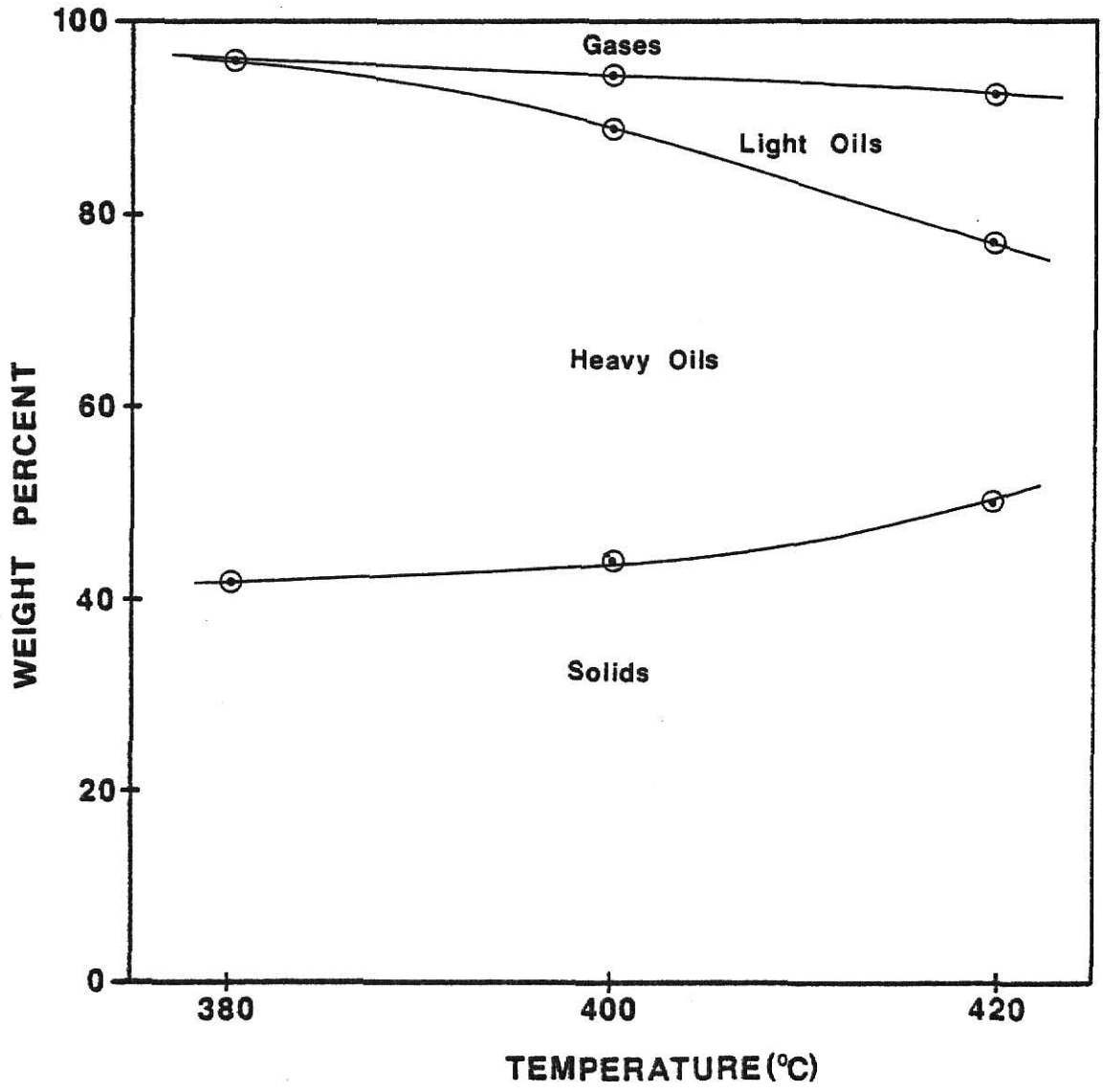


Figure 21. Effect of reaction temperature on product distribution:

Time = 60 minutes
Solvent-to-Coal ratio = 1:1.

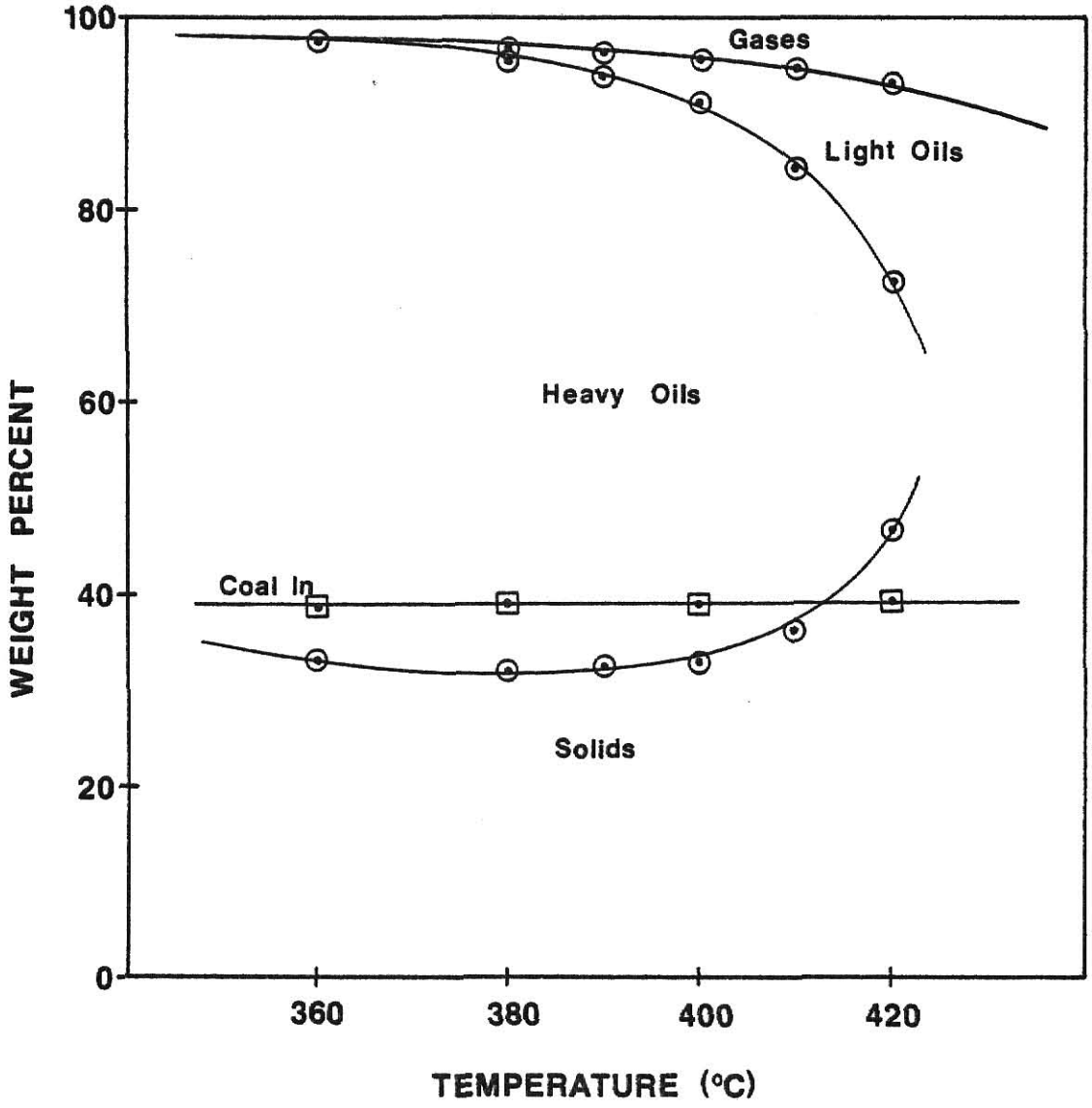


Figure 22. Effect of reaction temperature on product distribution:

Time = 60 minutes
Solvent-to-Coal ratio = 1.5:1.

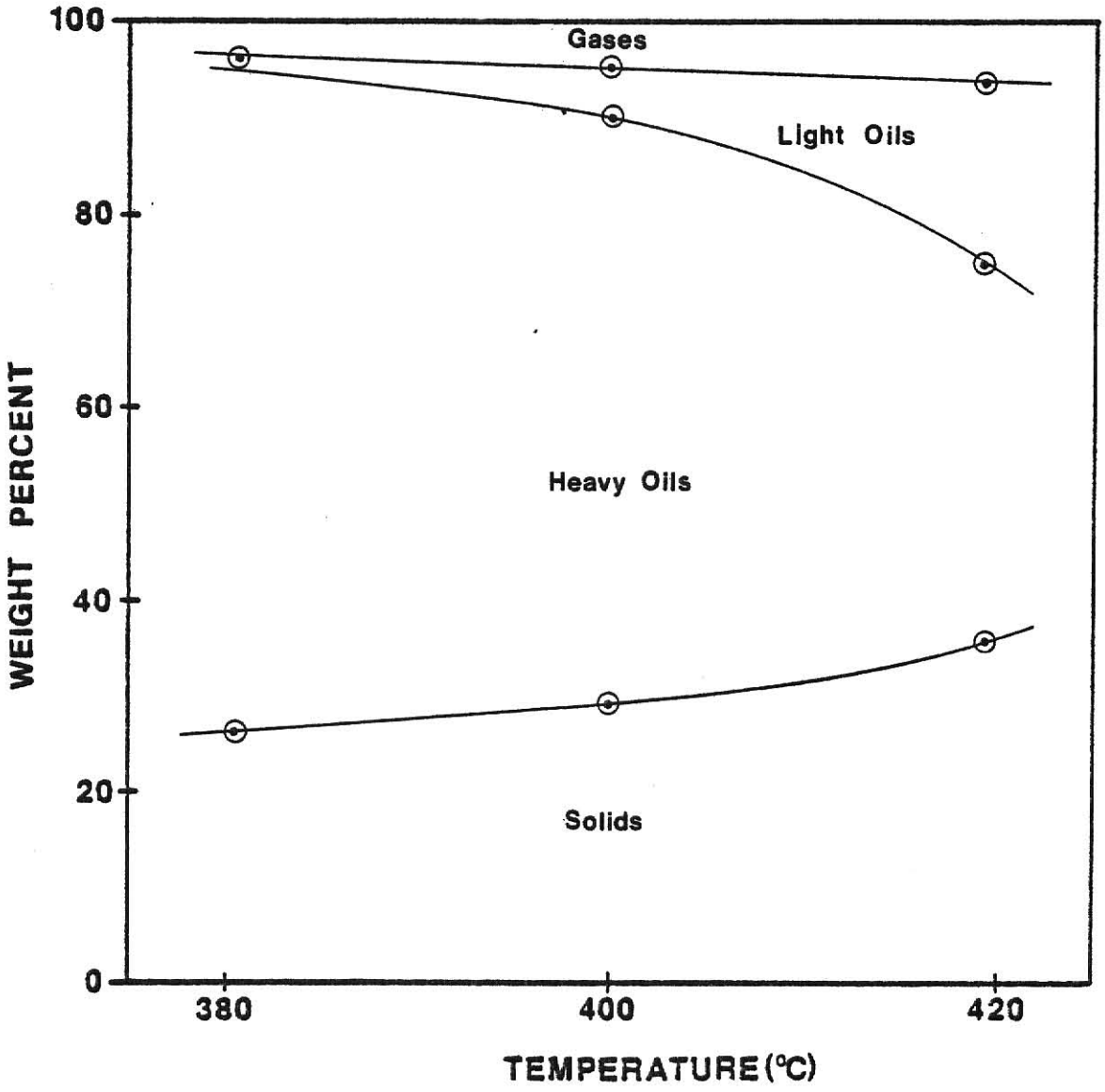


Figure 23. Effect of reaction temperature on product distribution:

Time = 60 minutes
Solvent-to-Coal ratio = 2:1.

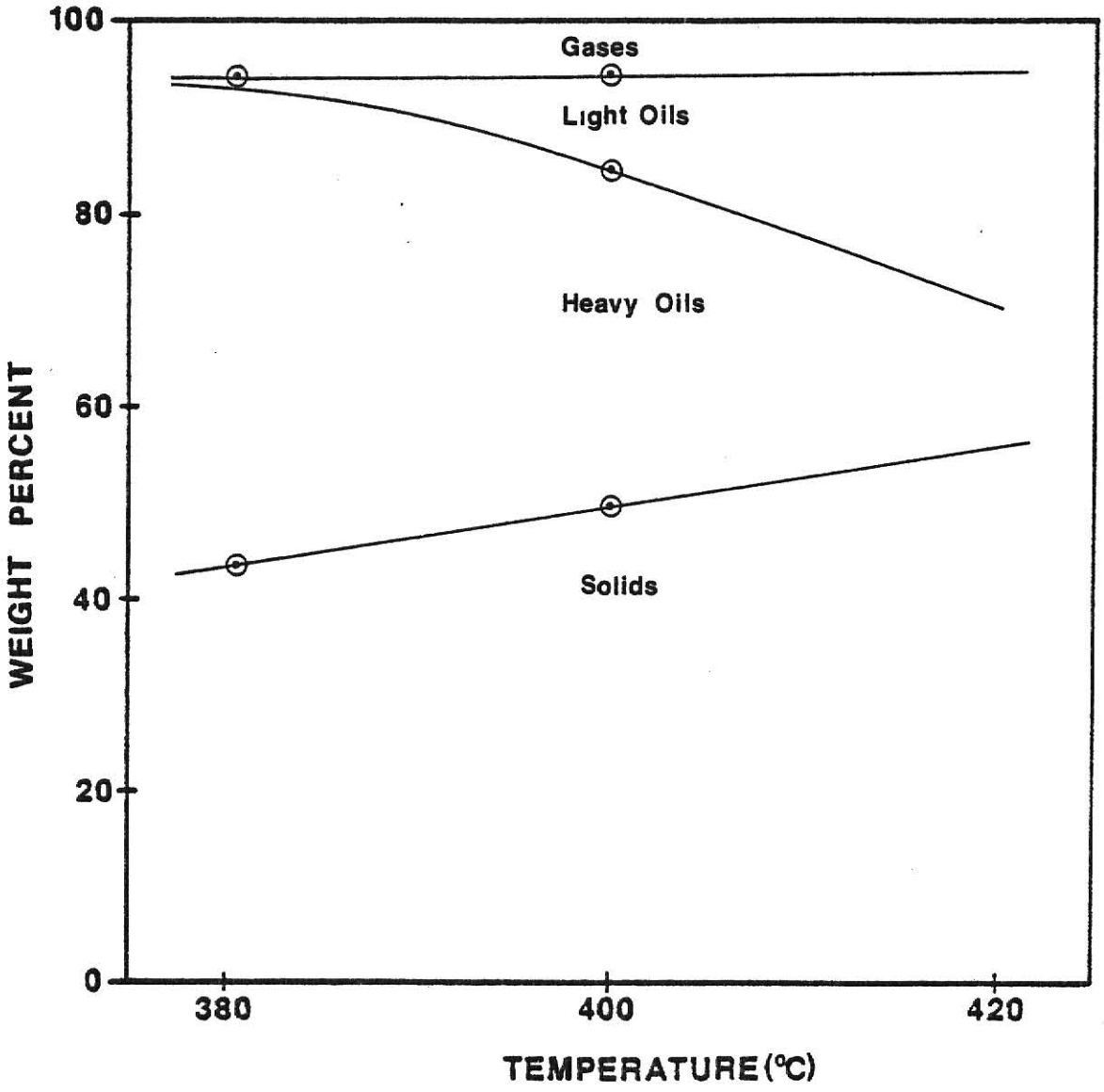


Figure 24. Effect of reaction temperature on product distribution:

Time = 90 minutes
Solvent-to-Coal ratio = 1:1.

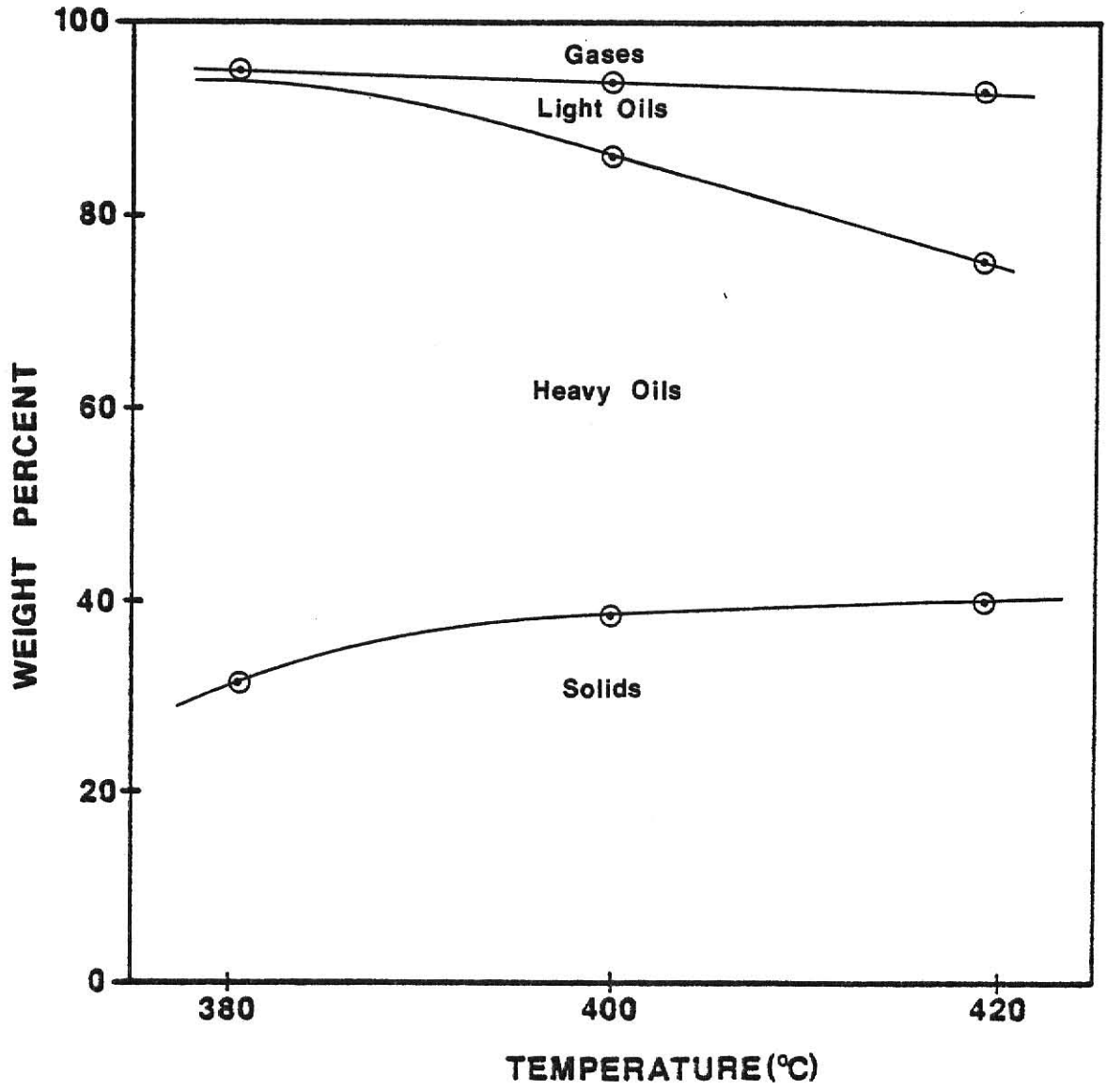


Figure 25. Effect of reaction temperature on product distribution:

Time = 90 minutes
Solvent-to-Coal ratio = 1.5:1.

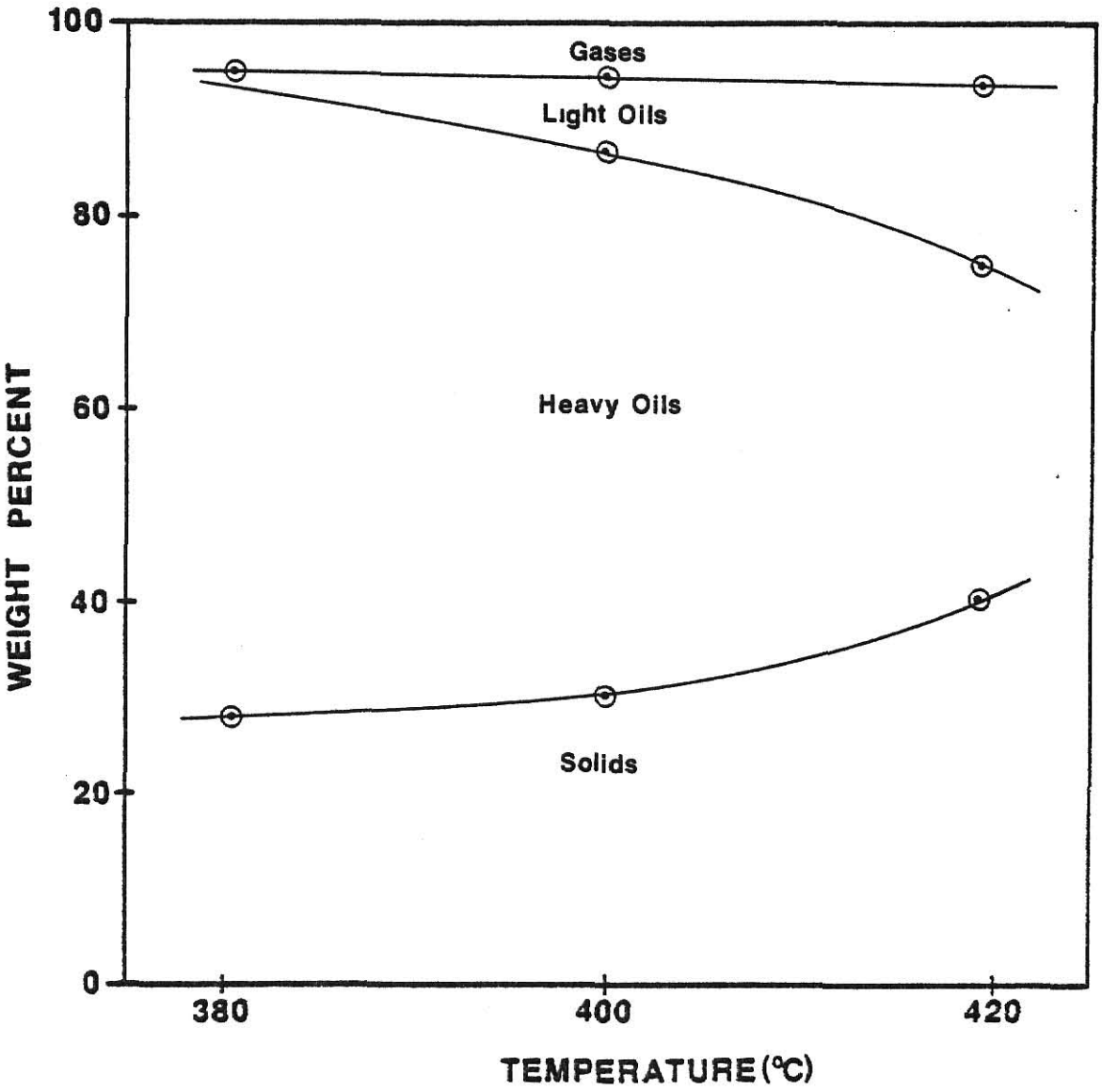


Figure 26. Effect of reaction temperature on product distribution:

Time = 90 minutes
Solvent-to-Coal ratio = 2:1.

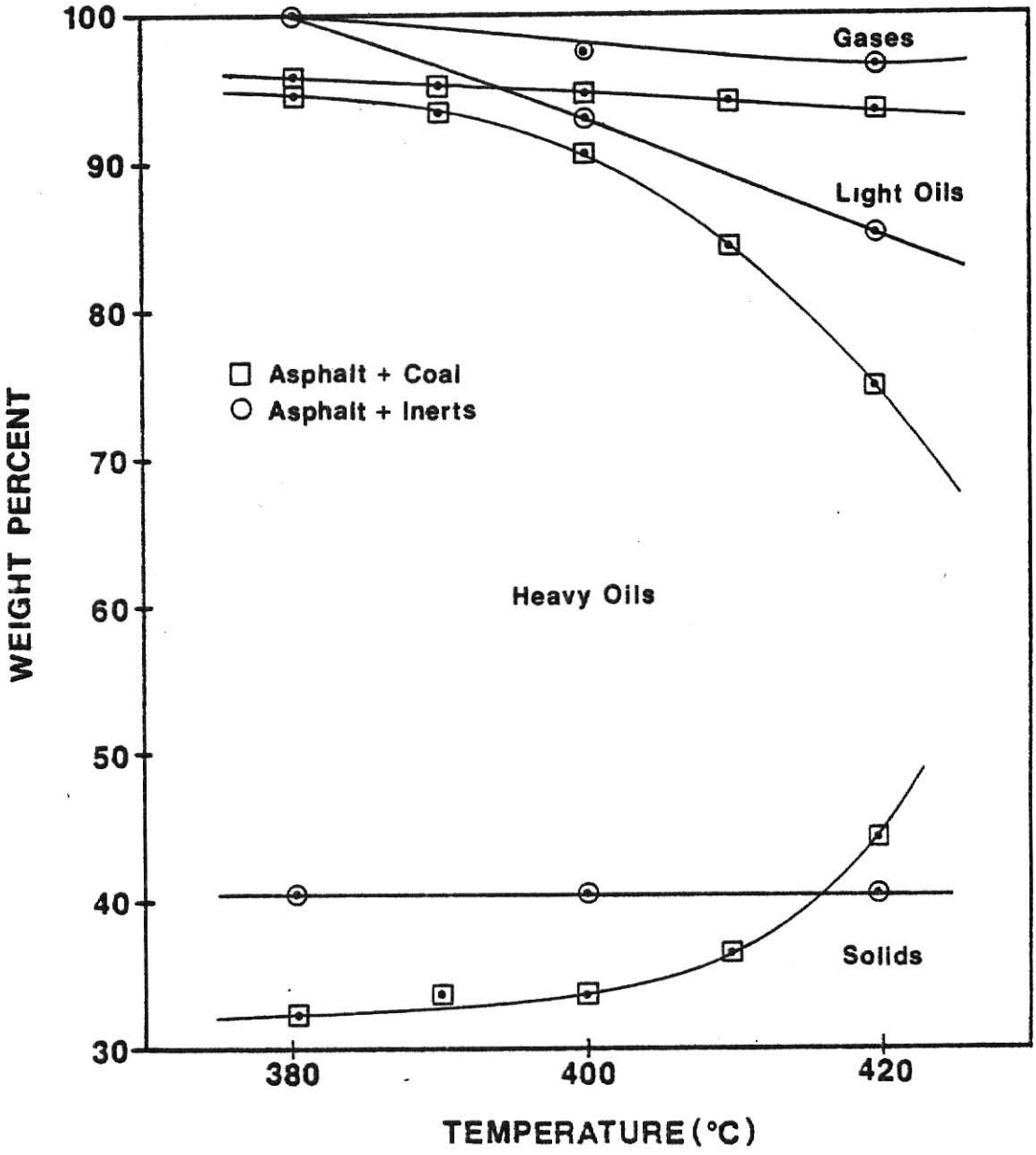


Figure 27. Effect of coal on product distribution

Time = 60 minutes
Solvent-to-Coal ratio = 1.5:1.

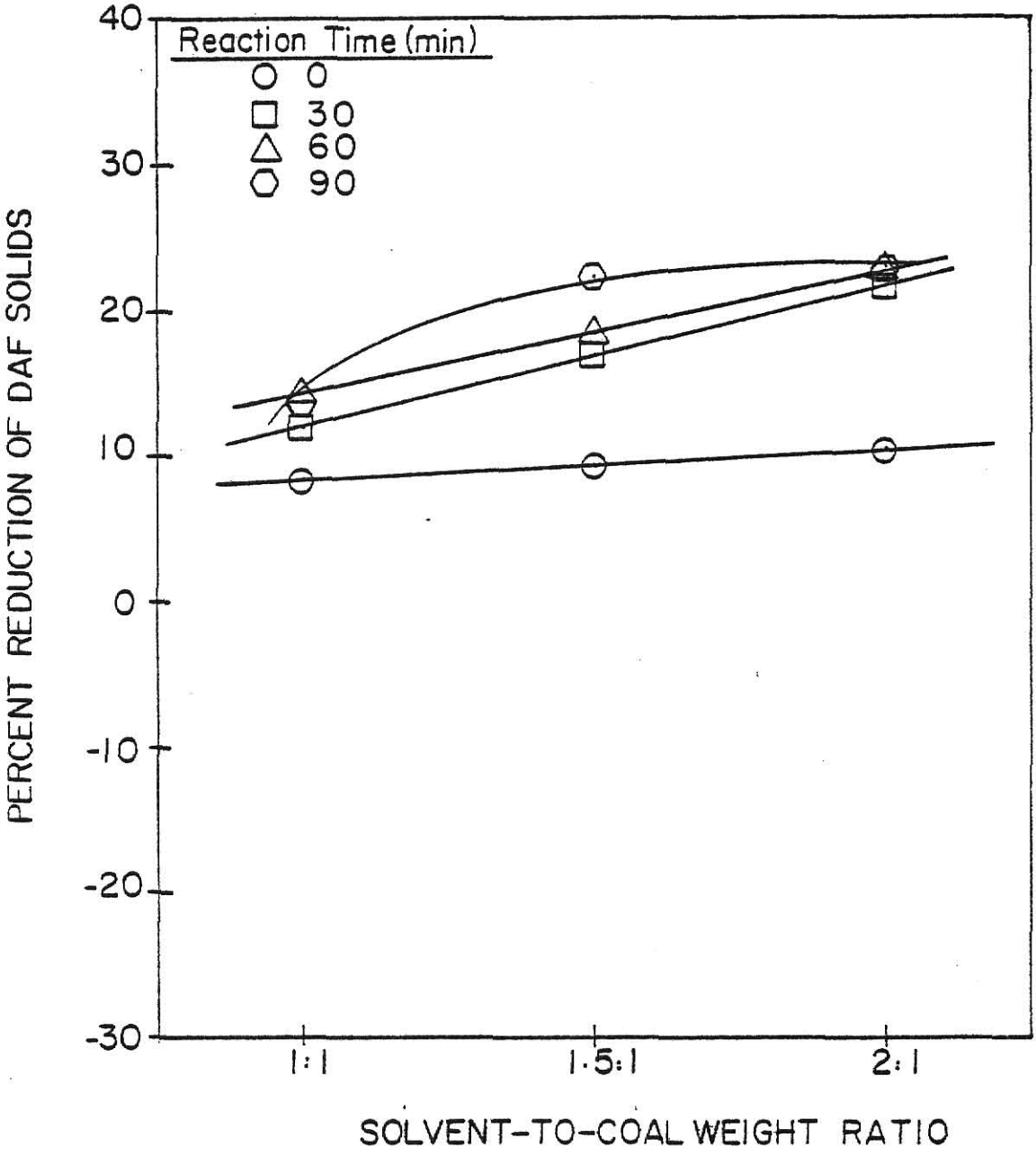


Figure 28. Effect of solvent-to-coal ratio on solids reduction:

Temperature = 380 °C (653 K).

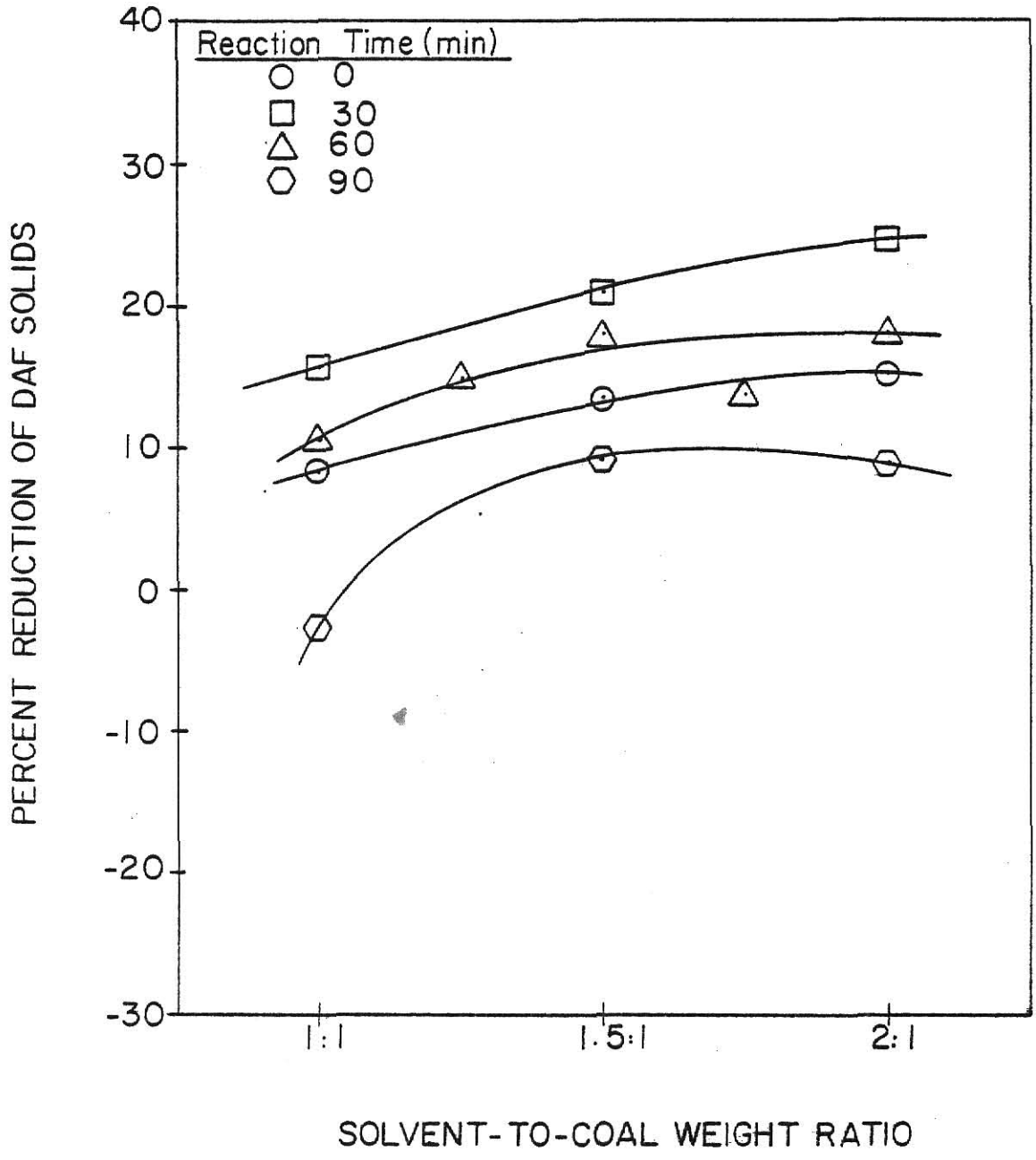


Figure 29. Effect of solvent-to-coal ratio on solids reduction:

Temperature = 400 $^{o}$C (673 K).

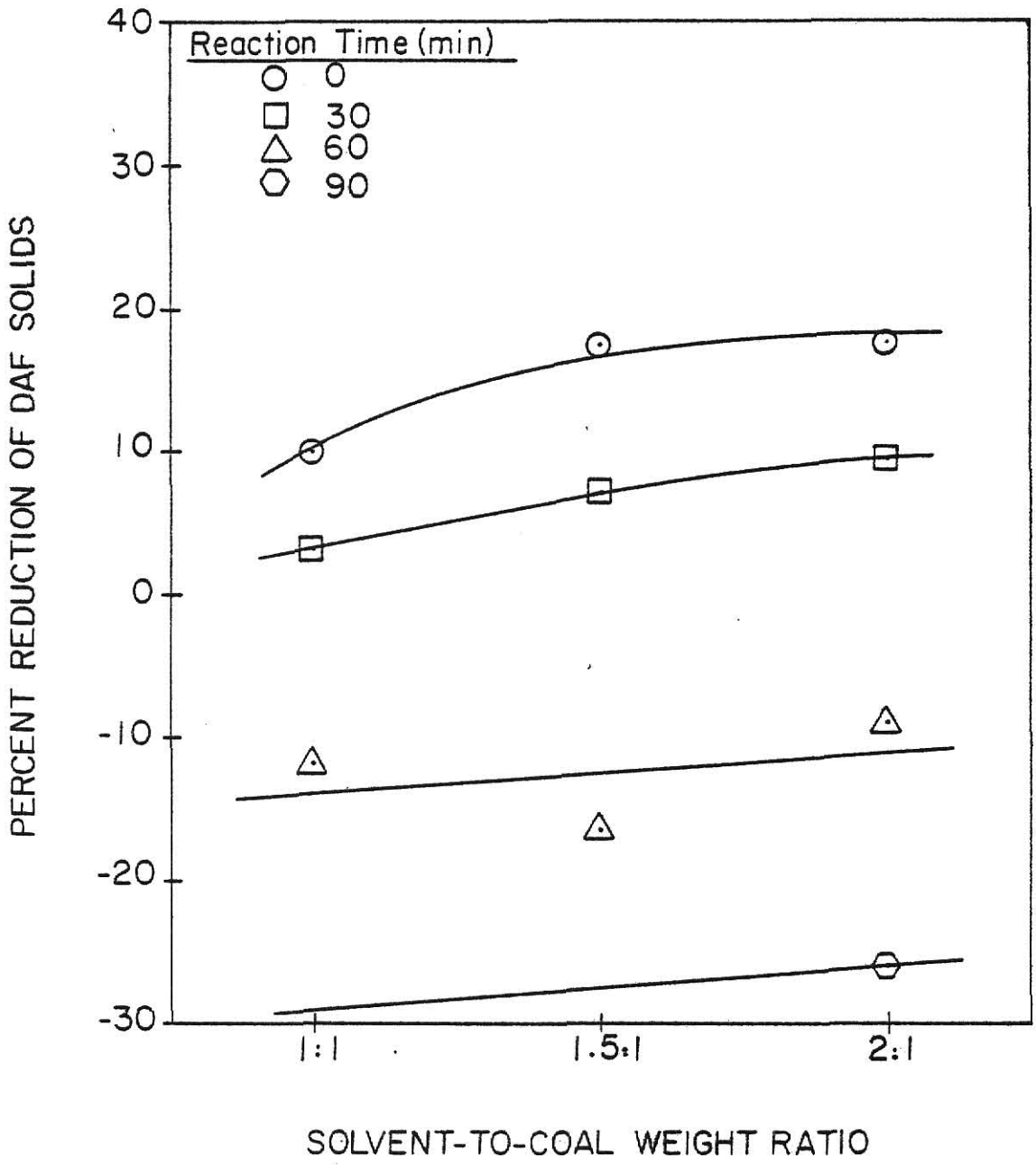


Figure 30. Effect of solvent-to-coal ratio on solids reduction:

Temperature = 420 °C (693 K).

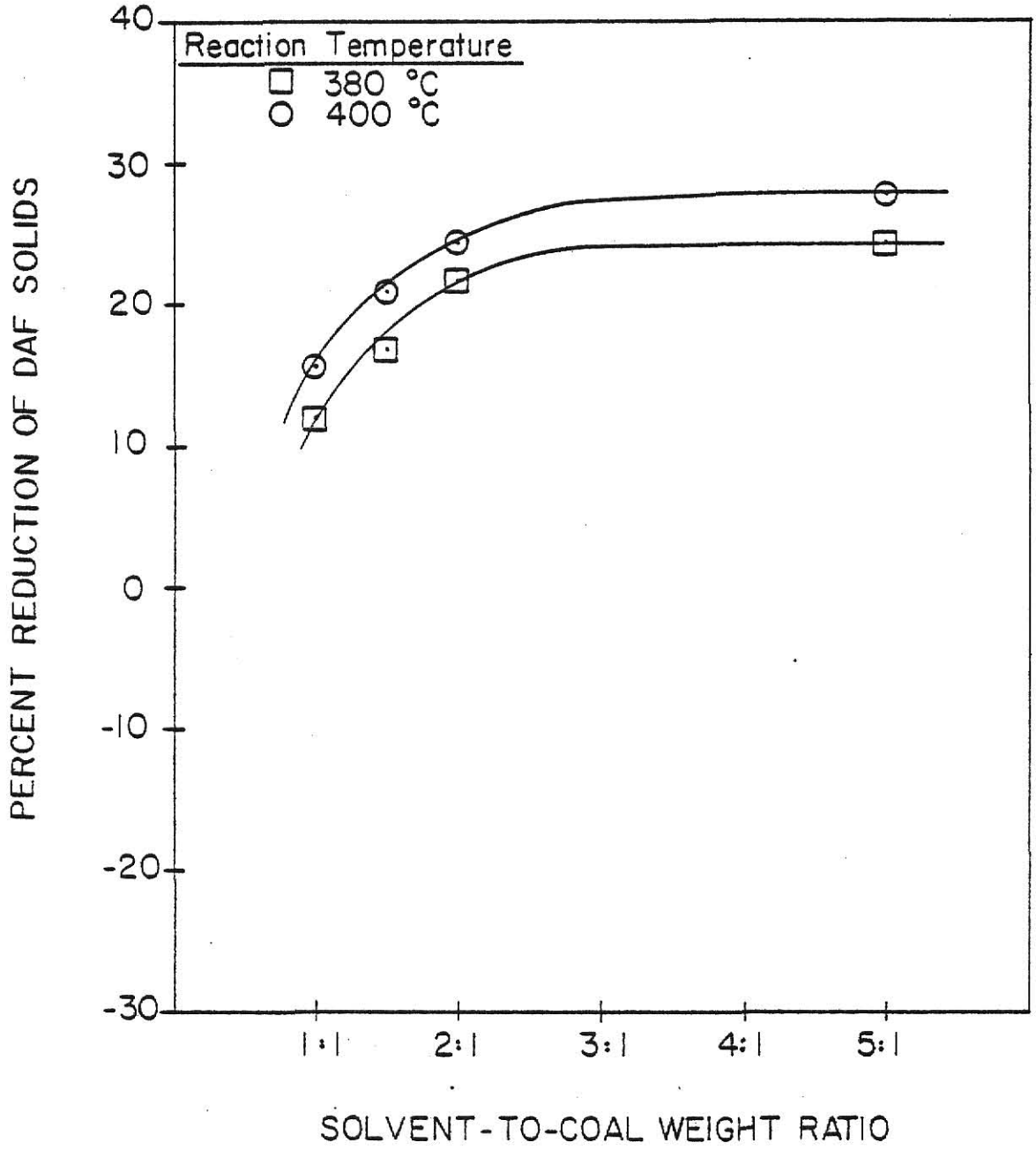


Figure 31. Effect of solvent-to-coal ratio on solids reduction:

Time = 30 minutes.

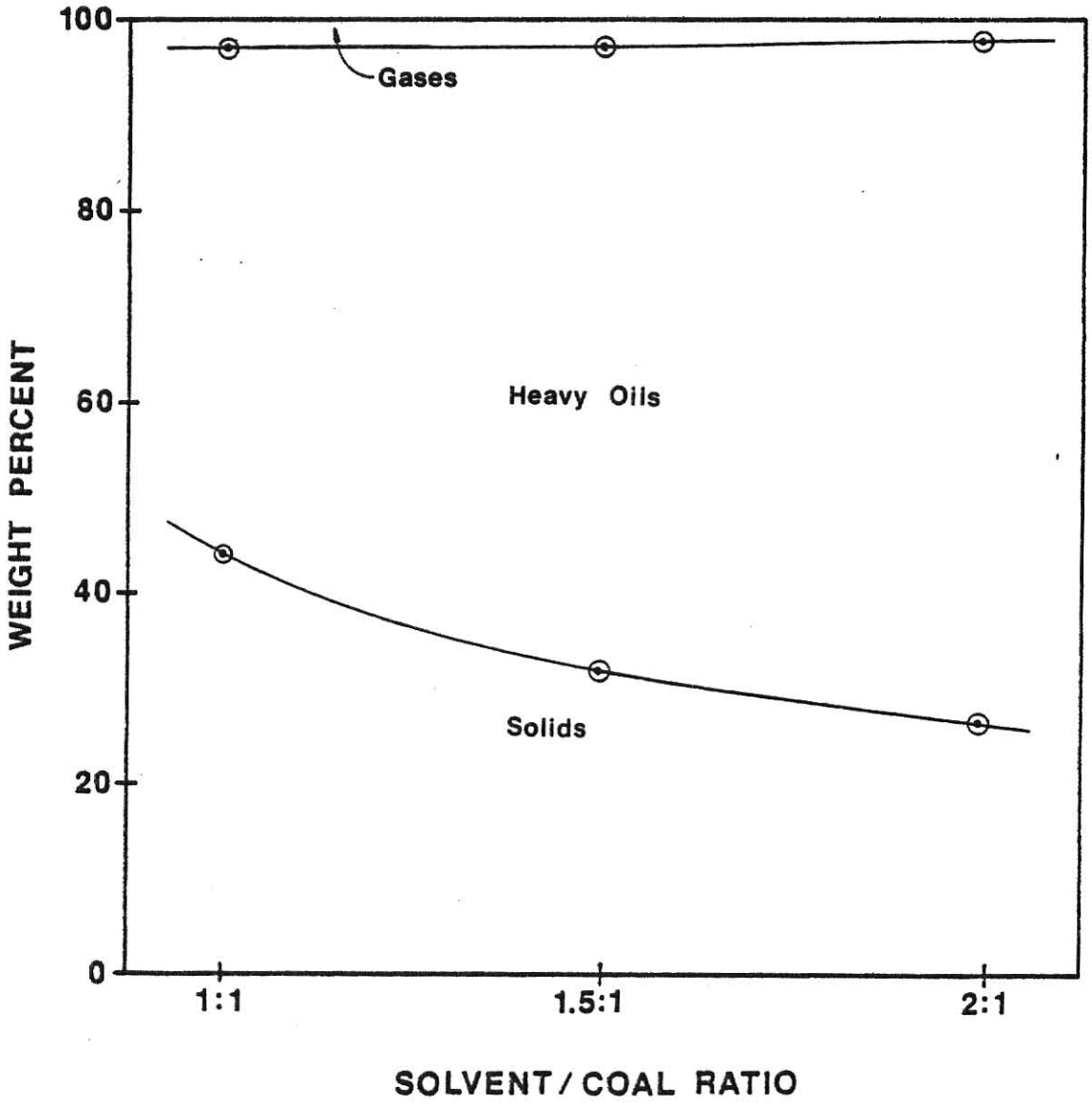


Figure 32. Effect of solvent-to-coal ratio on product distribution:

Temperature = 380 °C (653 K)
Time = 30 minutes.

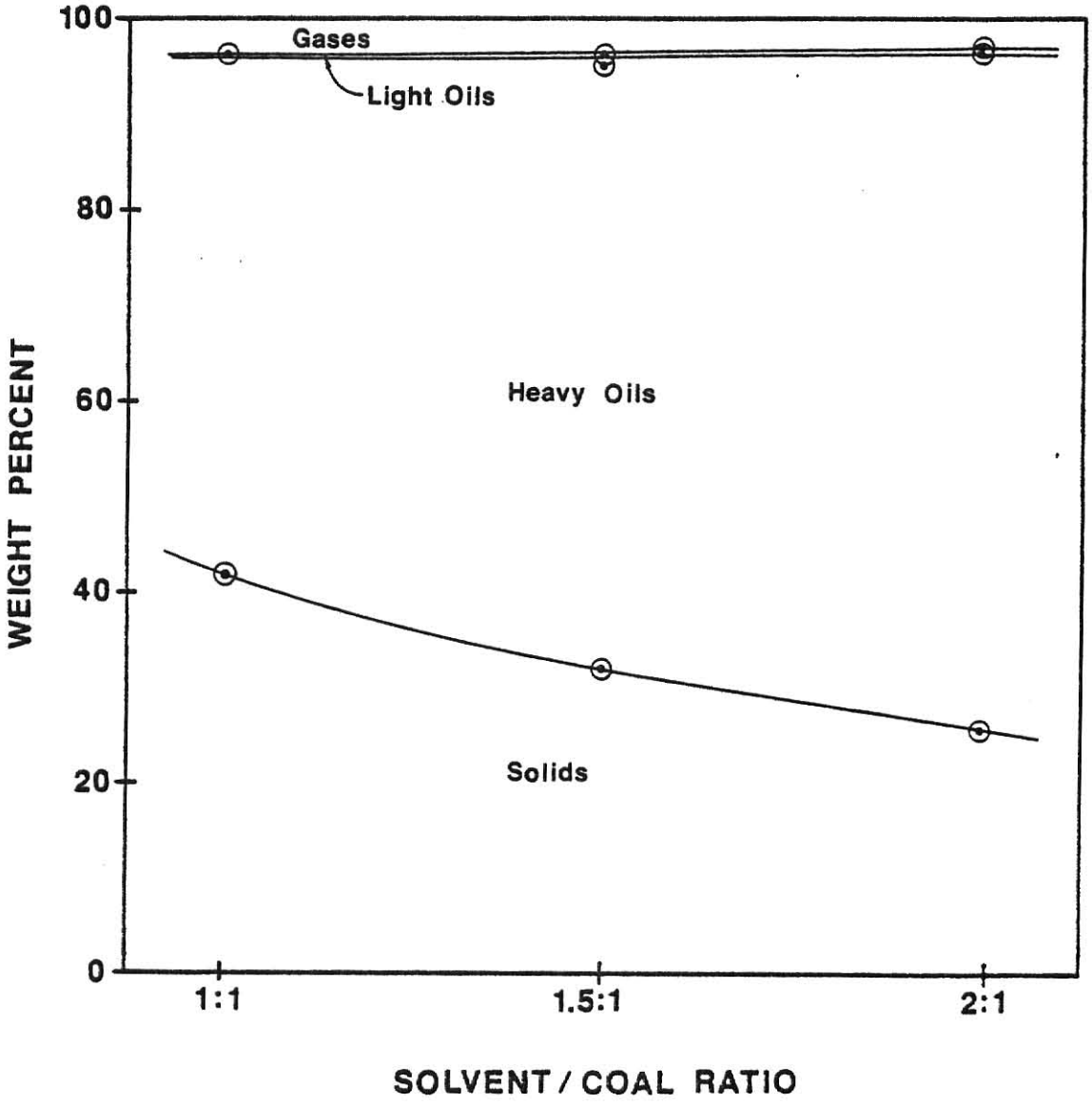


Figure 33. Effect of solvent-to-coal ratio on product distribution:

Temperature = 380 $^{o}$C (653 K)
Time = 60 minutes.

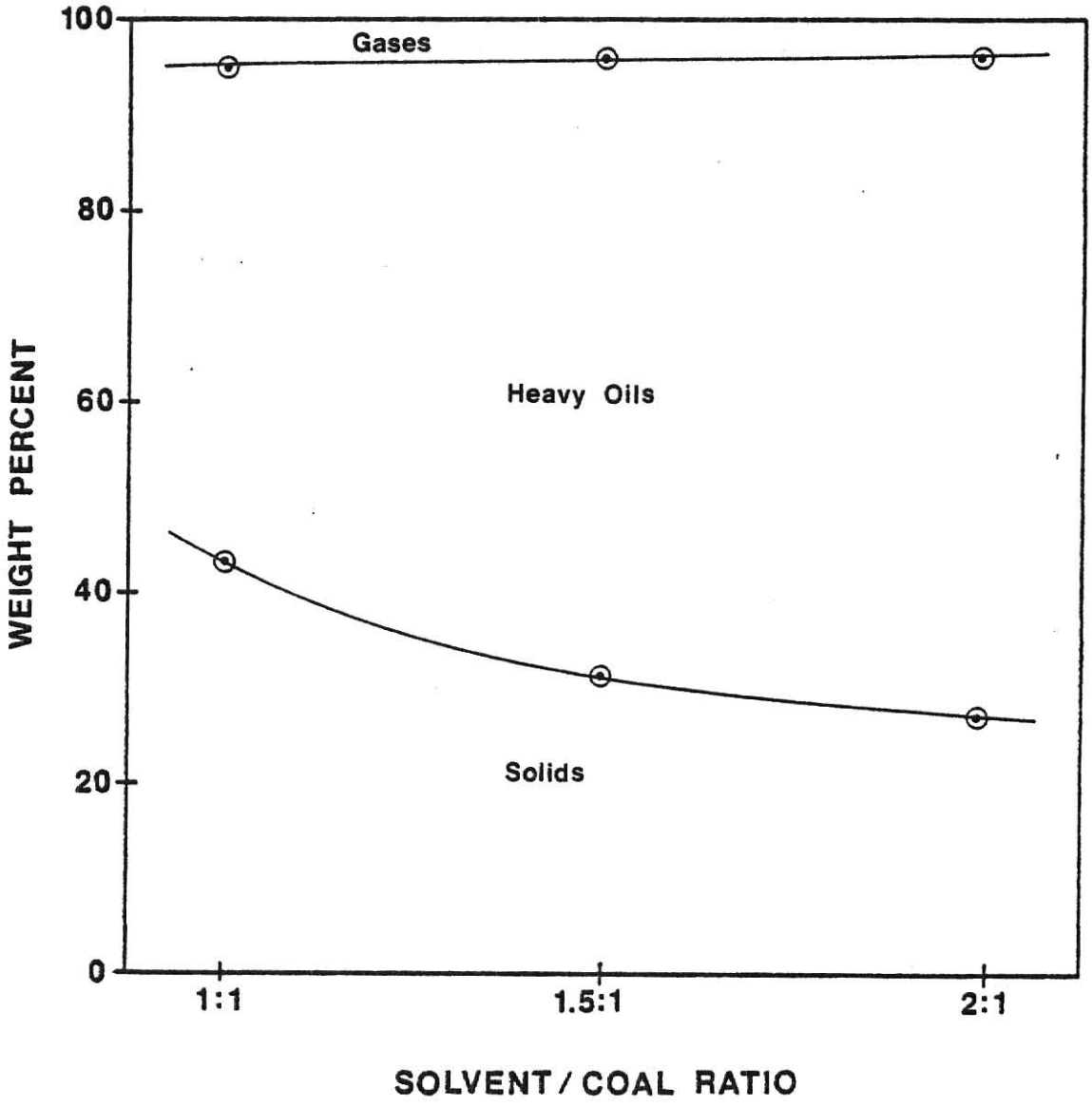


Figure 34. Effect of solvent-to-coal ratio on product distribution:

Temperature = 380 °C (653 K)
Time = 90 minutes.

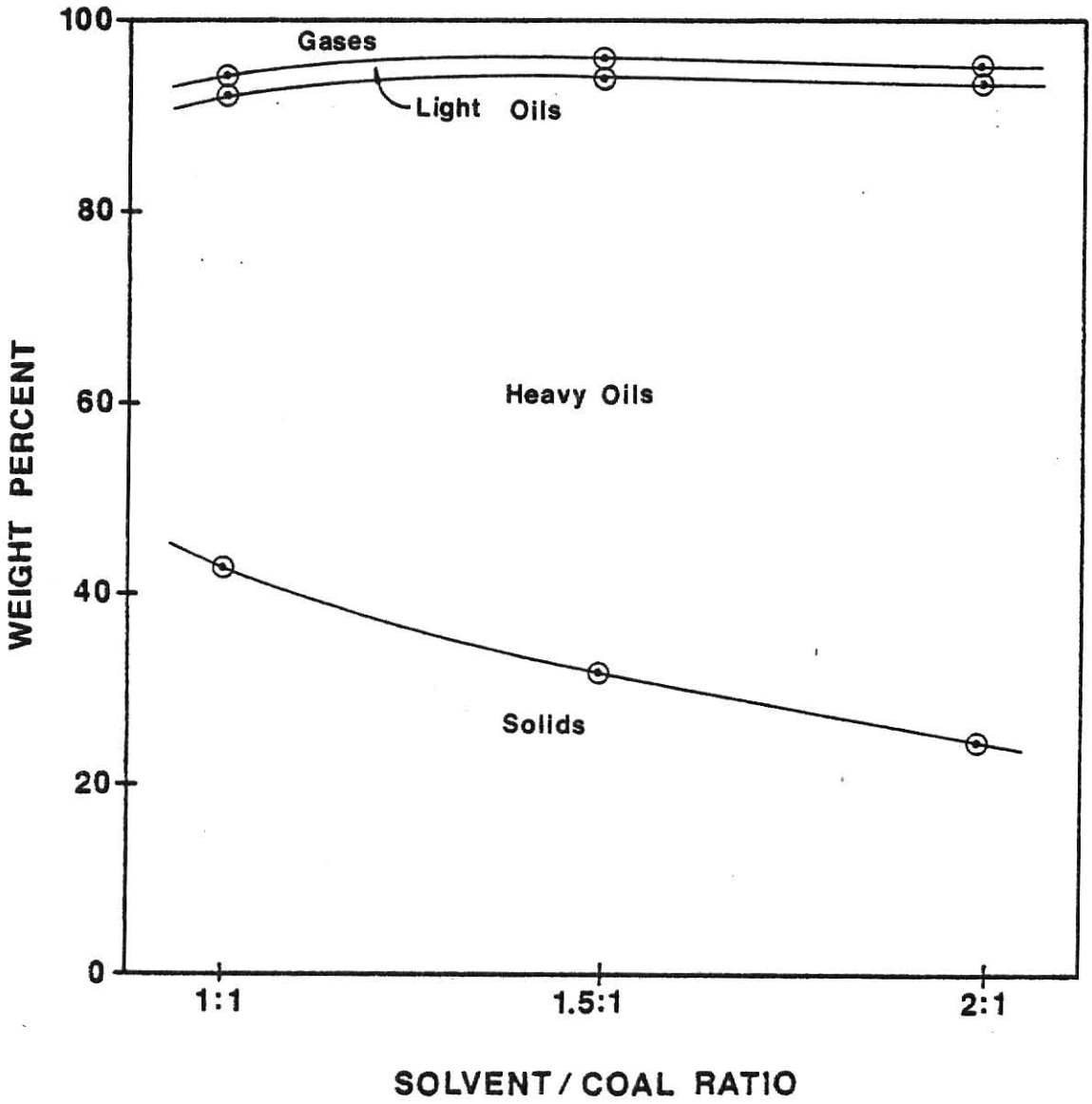


Figure 35. Effect of solvent-to-coal ratio on product distribution:

Temperature = 400 °C (673 K)
Time = 30 minutes.

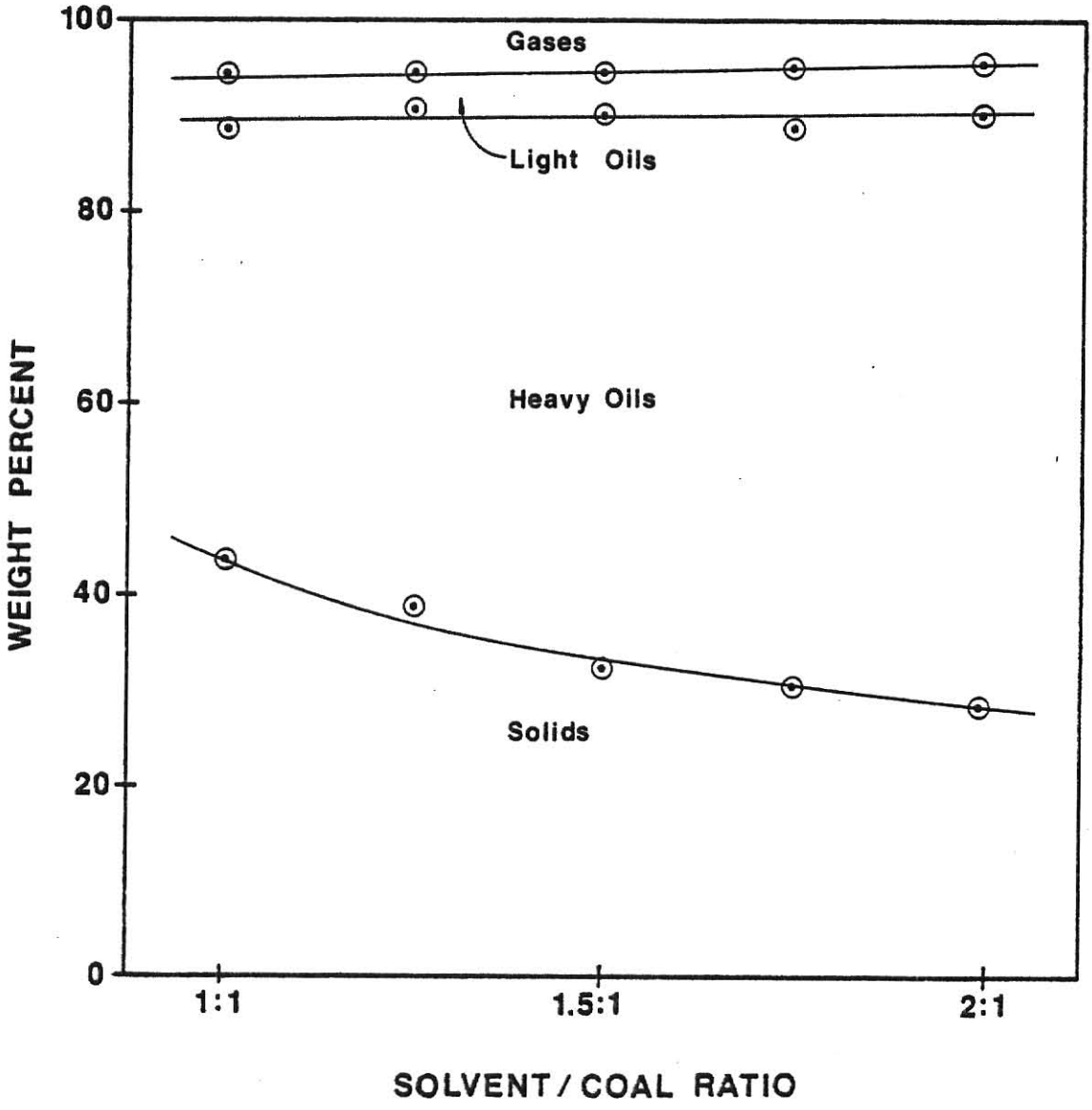


Figure 36. Effect of solvent-to-coal ratio on product distribution:

Temperature = 400 °C (673 K)
Time = 60 minutes.

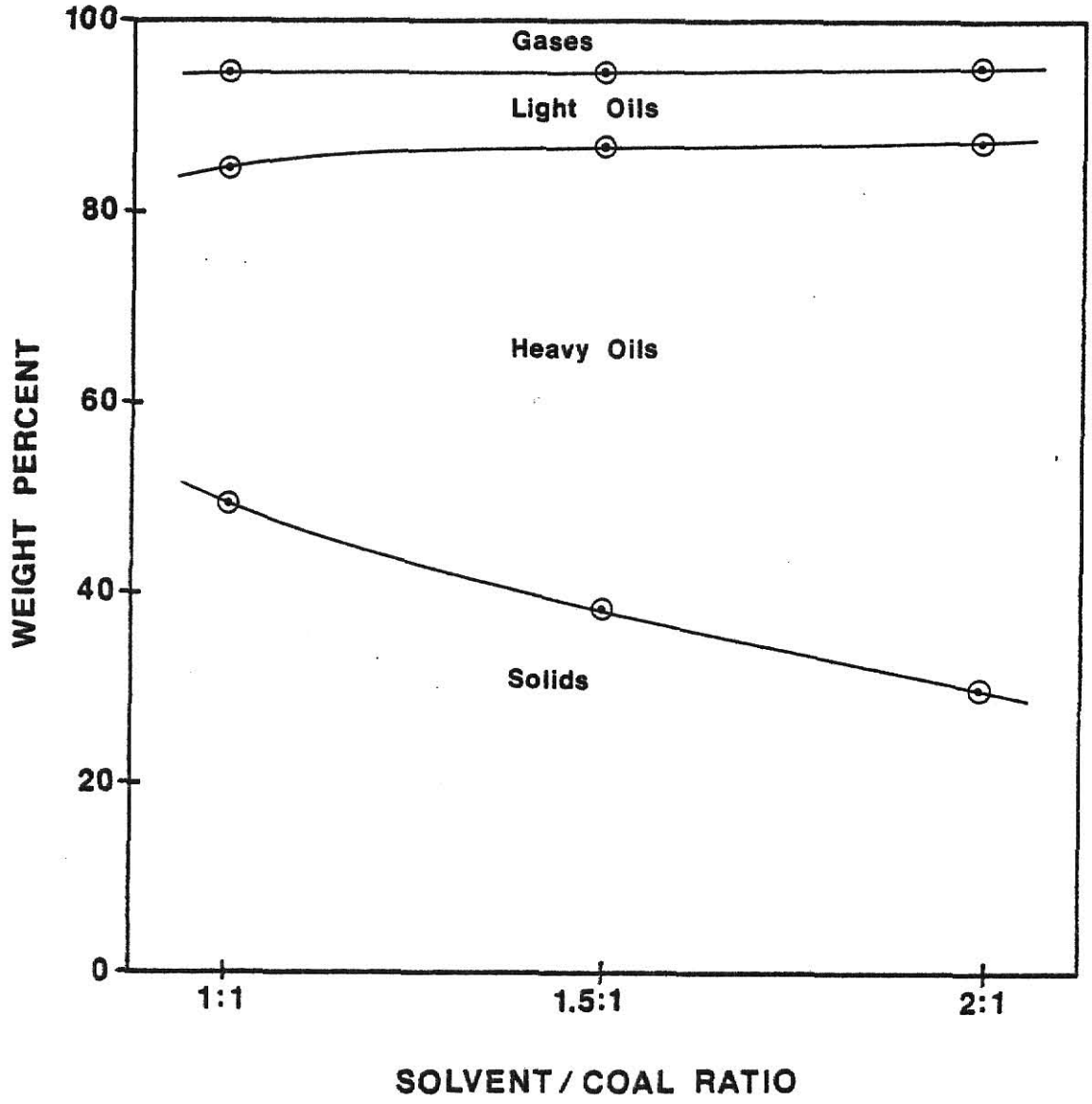


Figure 37. Effect of solvent-to-coal ratio on product distribution:

Temperature = 400 °C (673 K)
Time = 90 minutes.

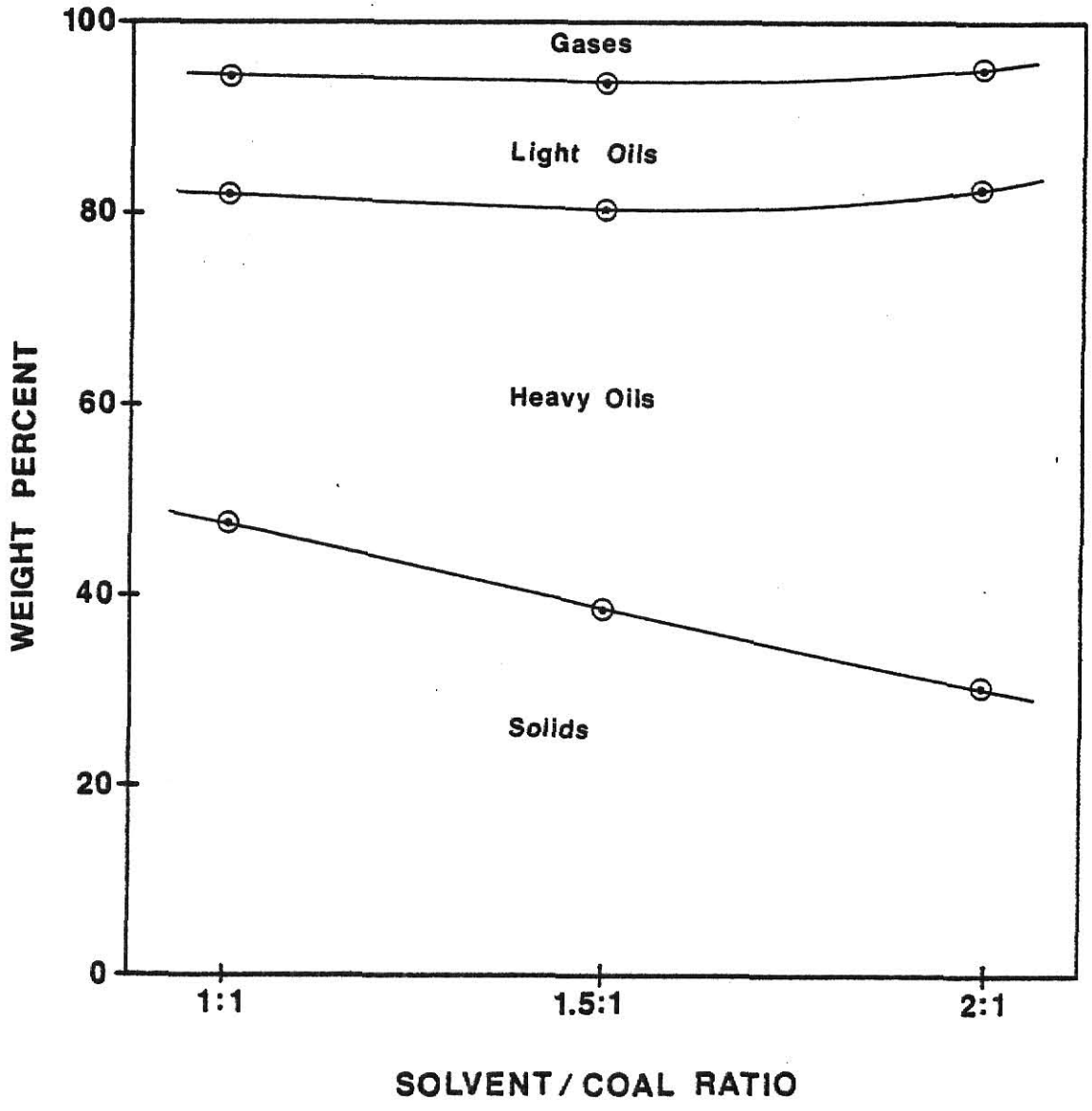


Figure 38. Effect of solvent-to-coal ratio on product distribution:

Temperature = 420 °C (693 K)
Time = 30 minutes.

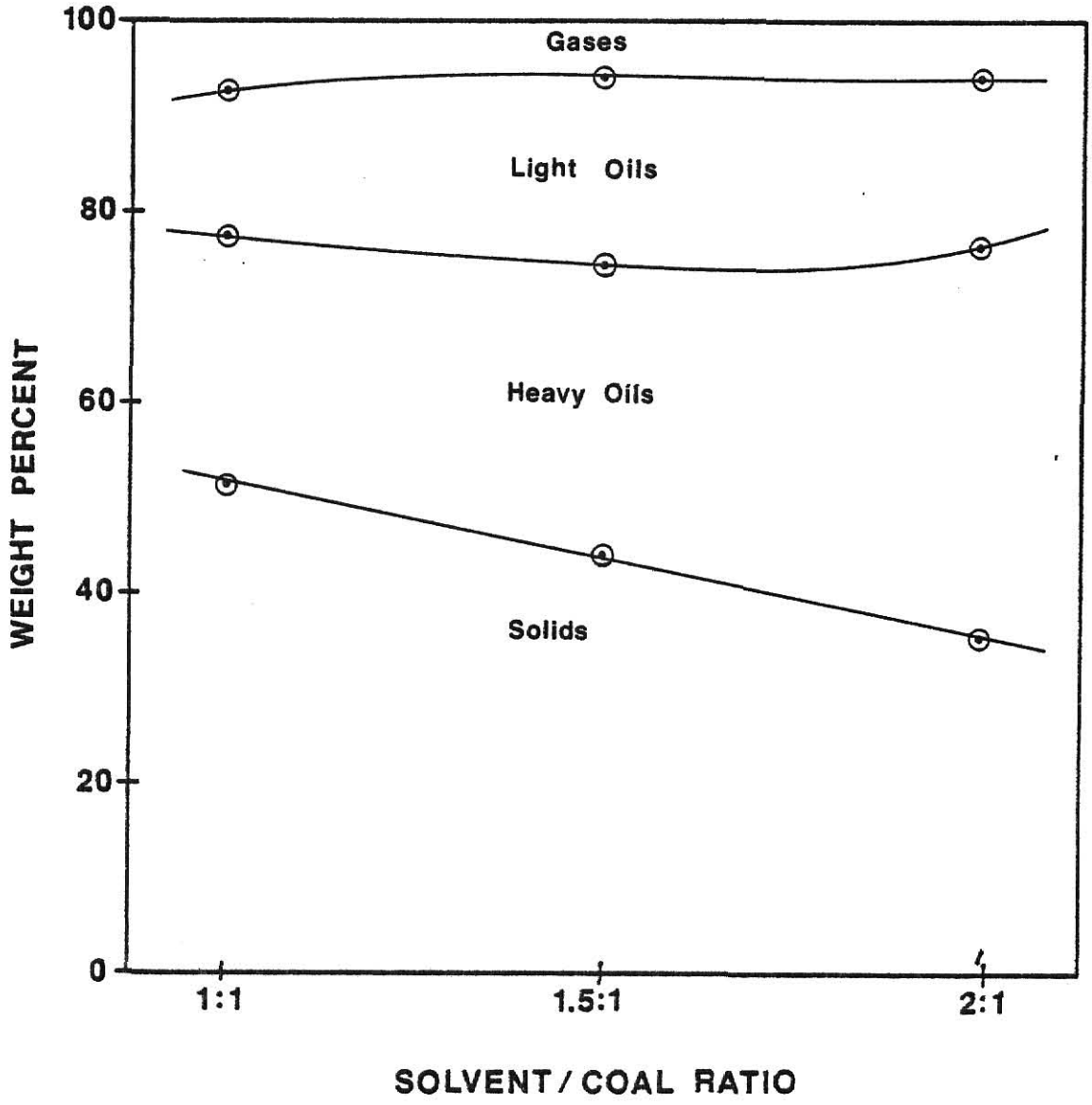


Figure 39. Effect of solvent-to-coal ratio on product distribution:

Temperature = 420 °C (693 K)
Time = 60 minutes.

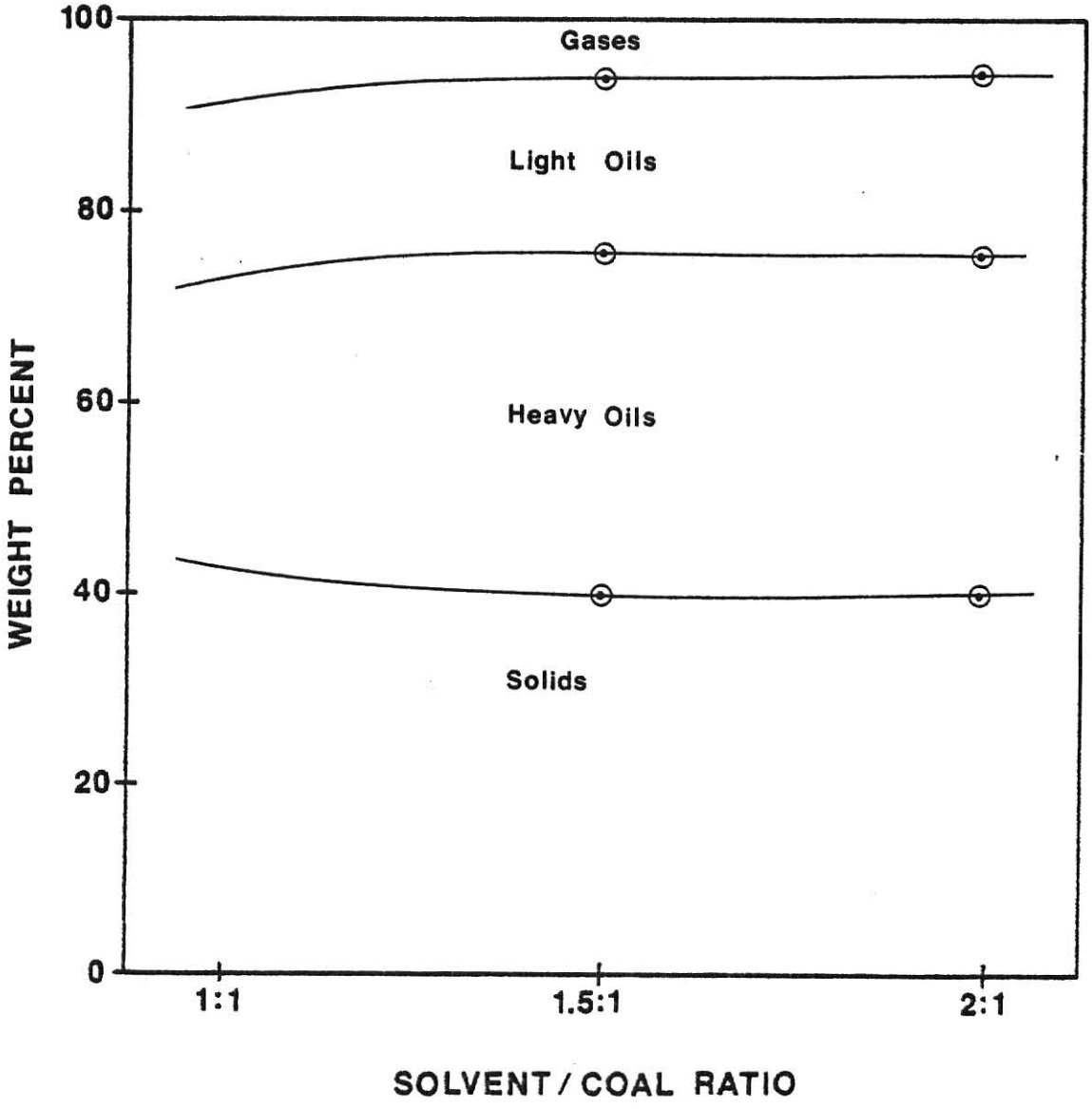


Figure 40. Effect of solvent-to-coal ratio on product distribution:

Temperature = 420 $^{o}$C (693 K)
Time = 90 minutes.

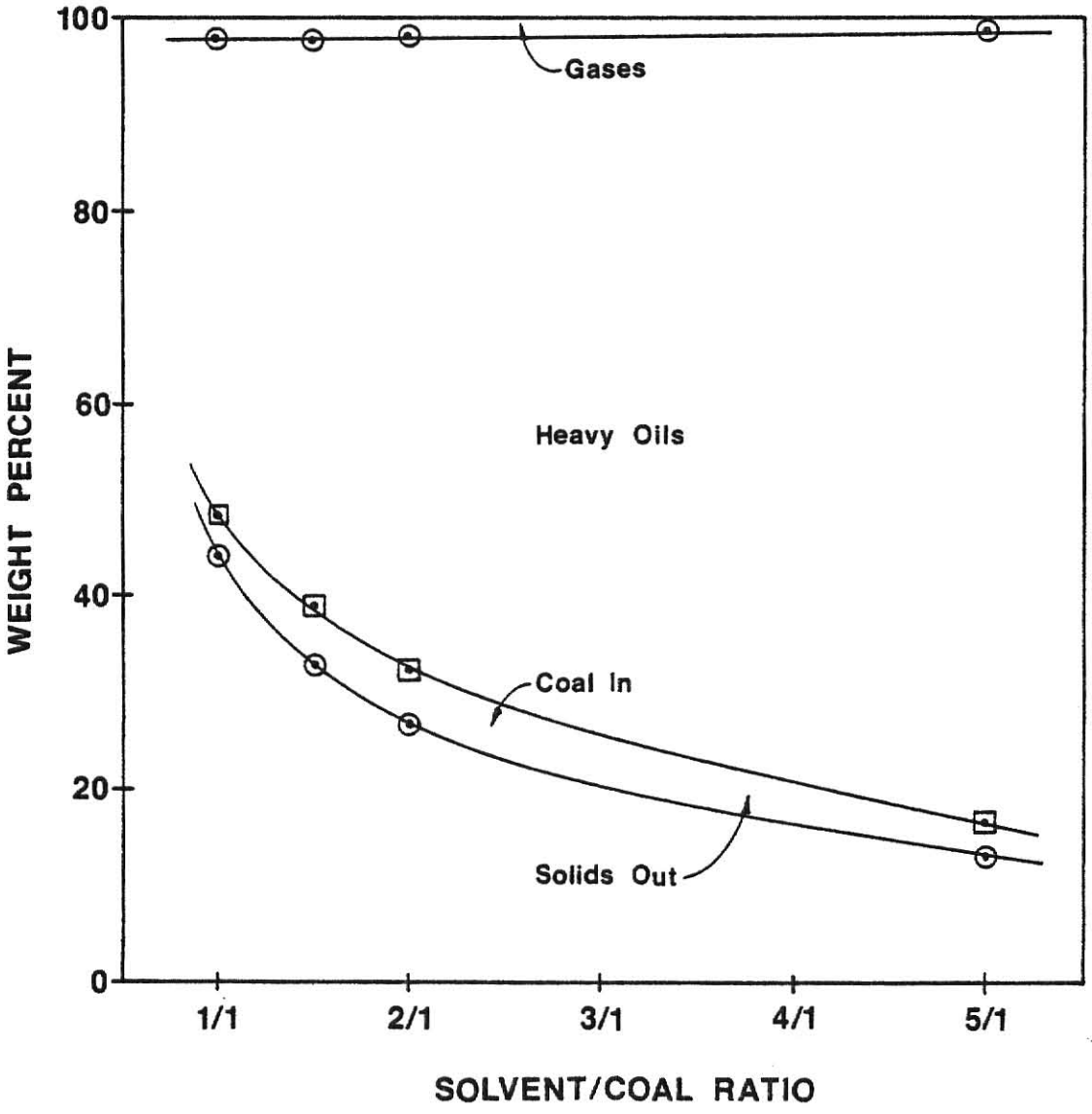


Figure 41. Effect of solvent-to-coal ratio on product distribution:

Temperature = 380 °C (653 K)
Time = 30 minutes.

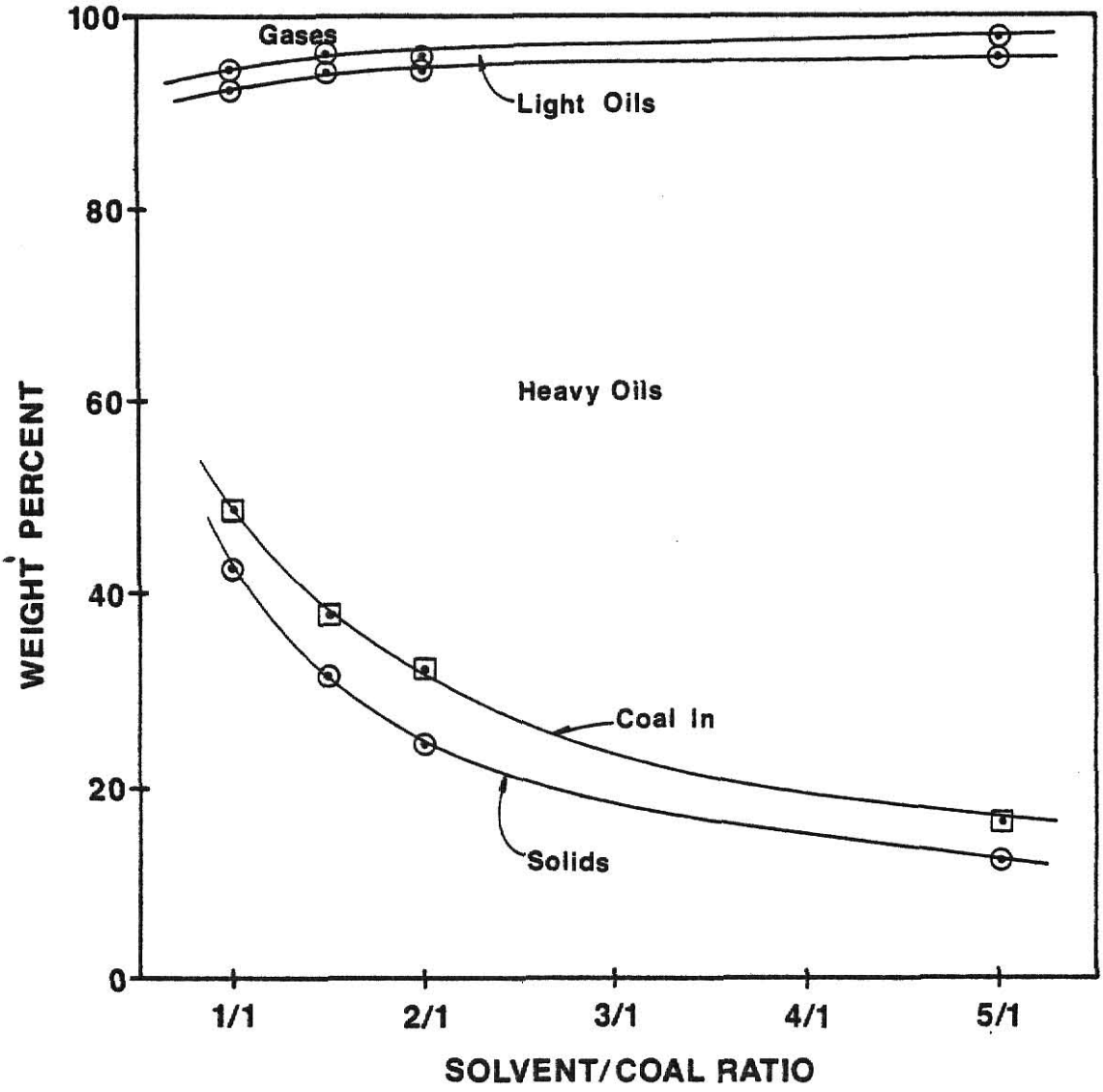


Figure 42. Effect of solvent-to-coal ratio on product distribution:

Temperature = 400 °C (673 K)
Time = 30 minutes.

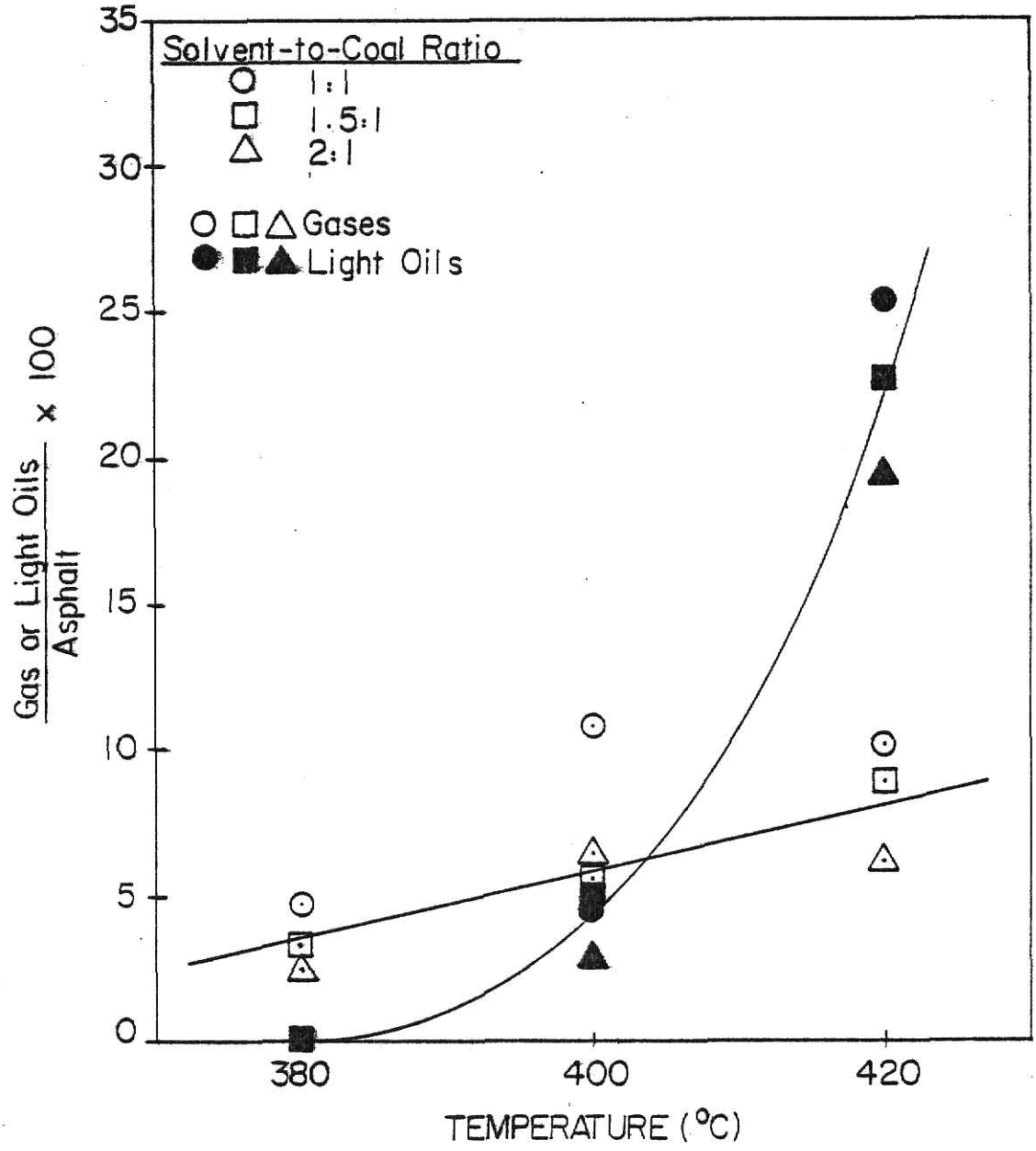


Figure 43. Proportional amounts of gases and light oils produced based on asphalt charged:

Time = 30 minutes.

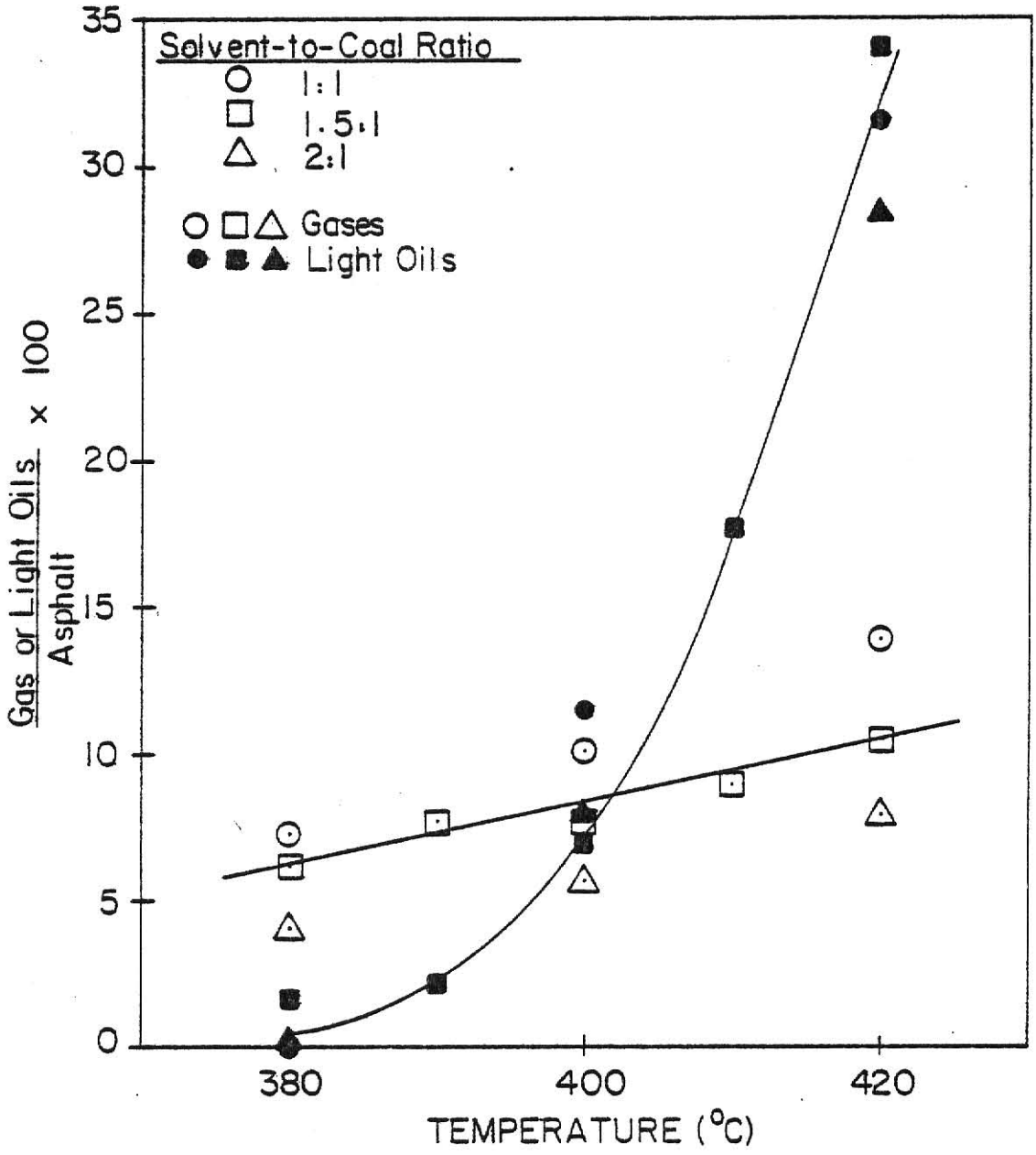


Figure 44. Proportional amounts of gases and light oils produced based on asphalt charged:

Time = 60 minutes.

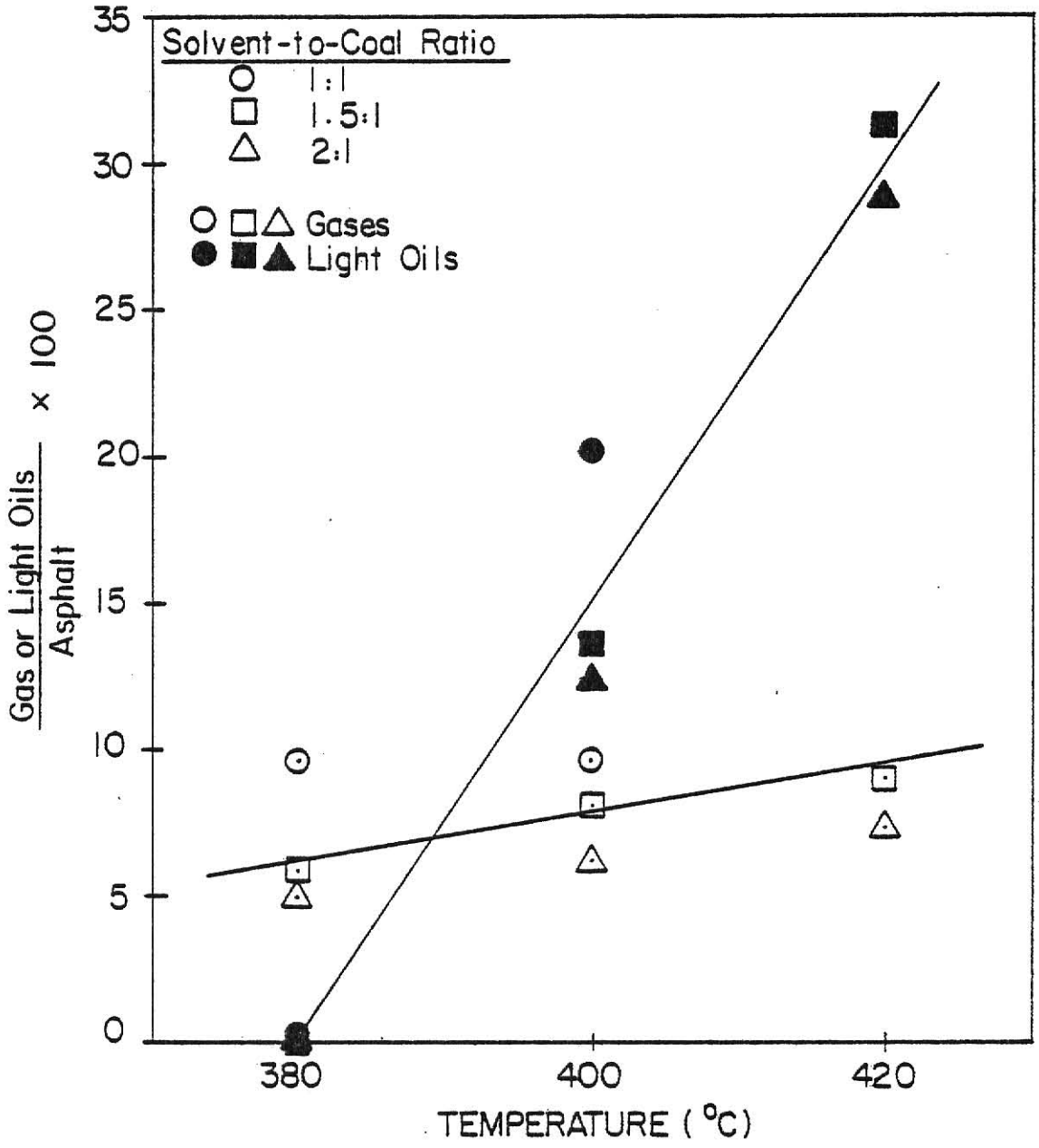


Figure 45. Proportional amounts of gases and light oils produced based on asphalt charged:

Time = 90 minutes.

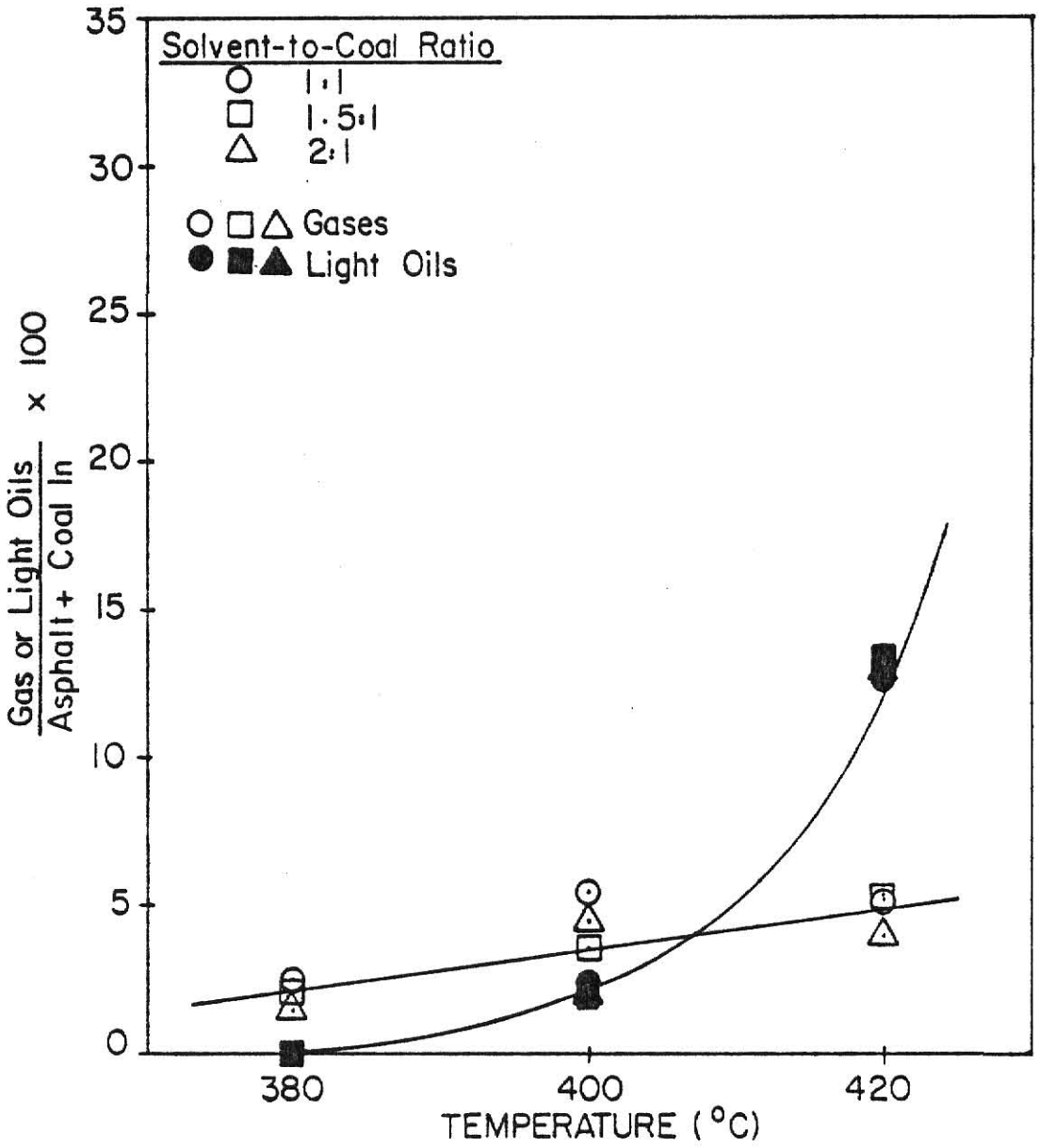


Figure 46. Proportional amounts of gases and light oils produced based on coal and asphalt charged:

Time = 30 minutes.

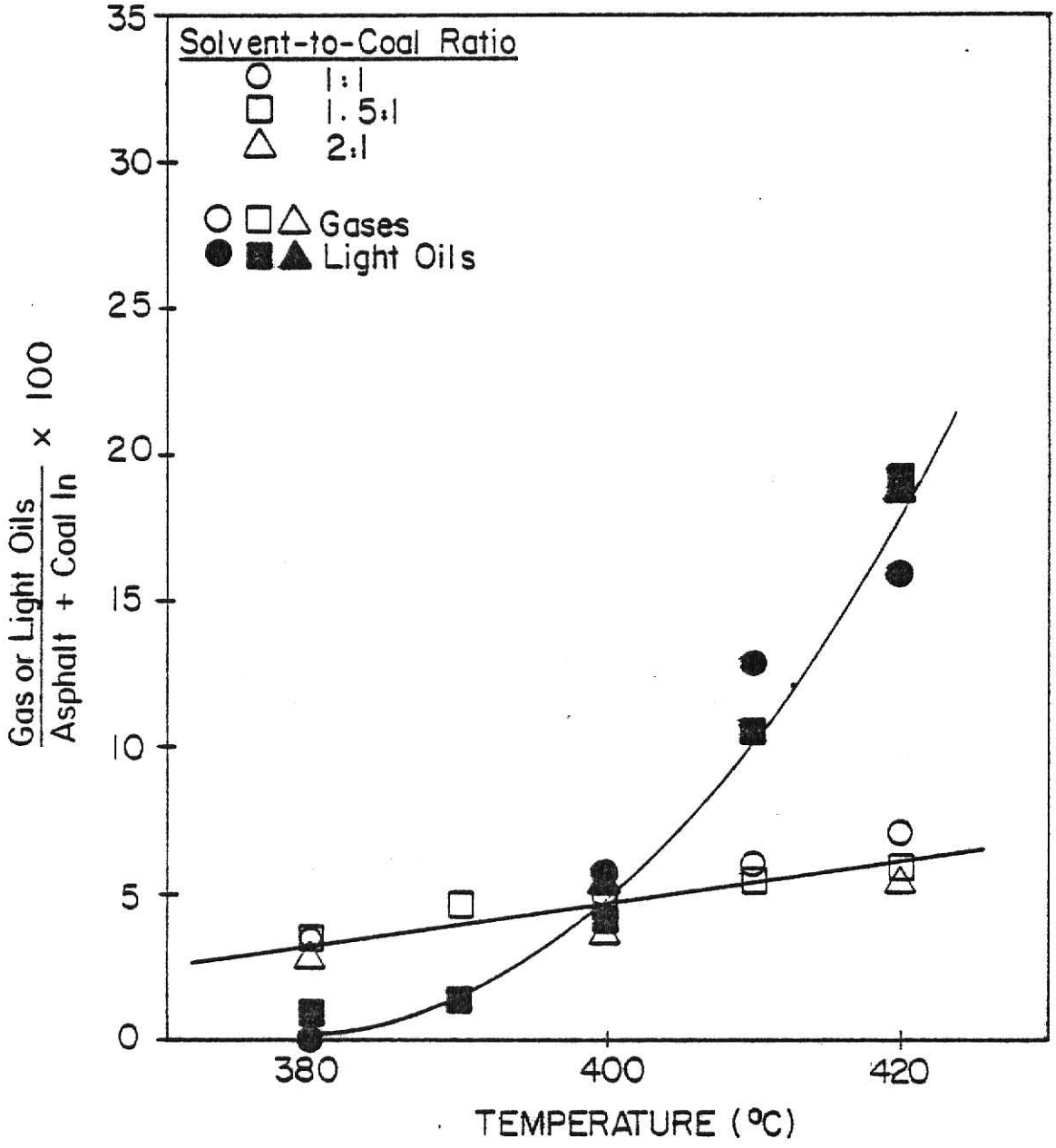


Figure 47. Proportional amounts of gases and light oils produced based on coal and asphalt charged:

Time = 60 minutes.

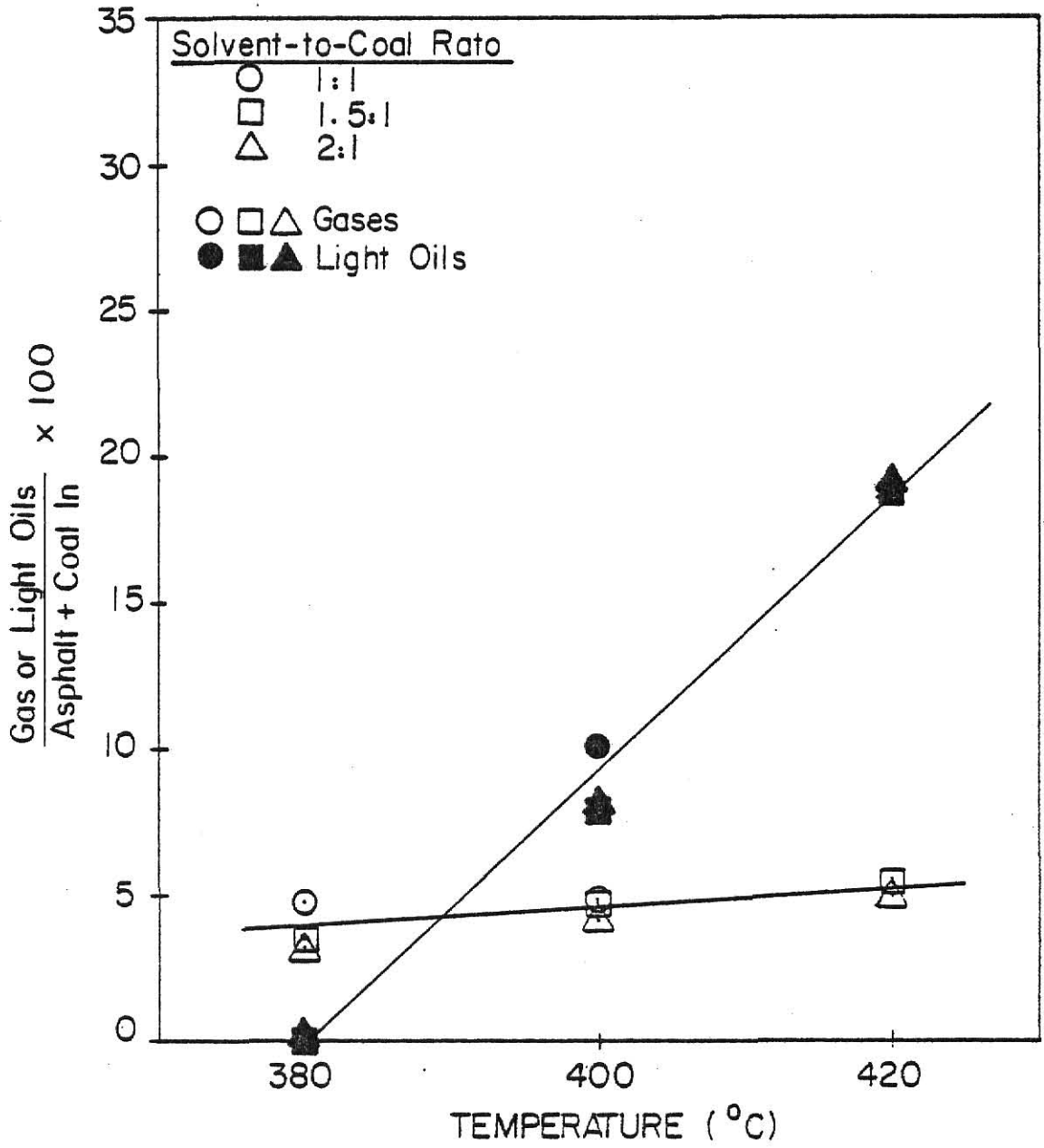


Figure 48. Proportional amounts of gases and light oils produced based on coal and asphalt charged:

Time = 90 minutes.

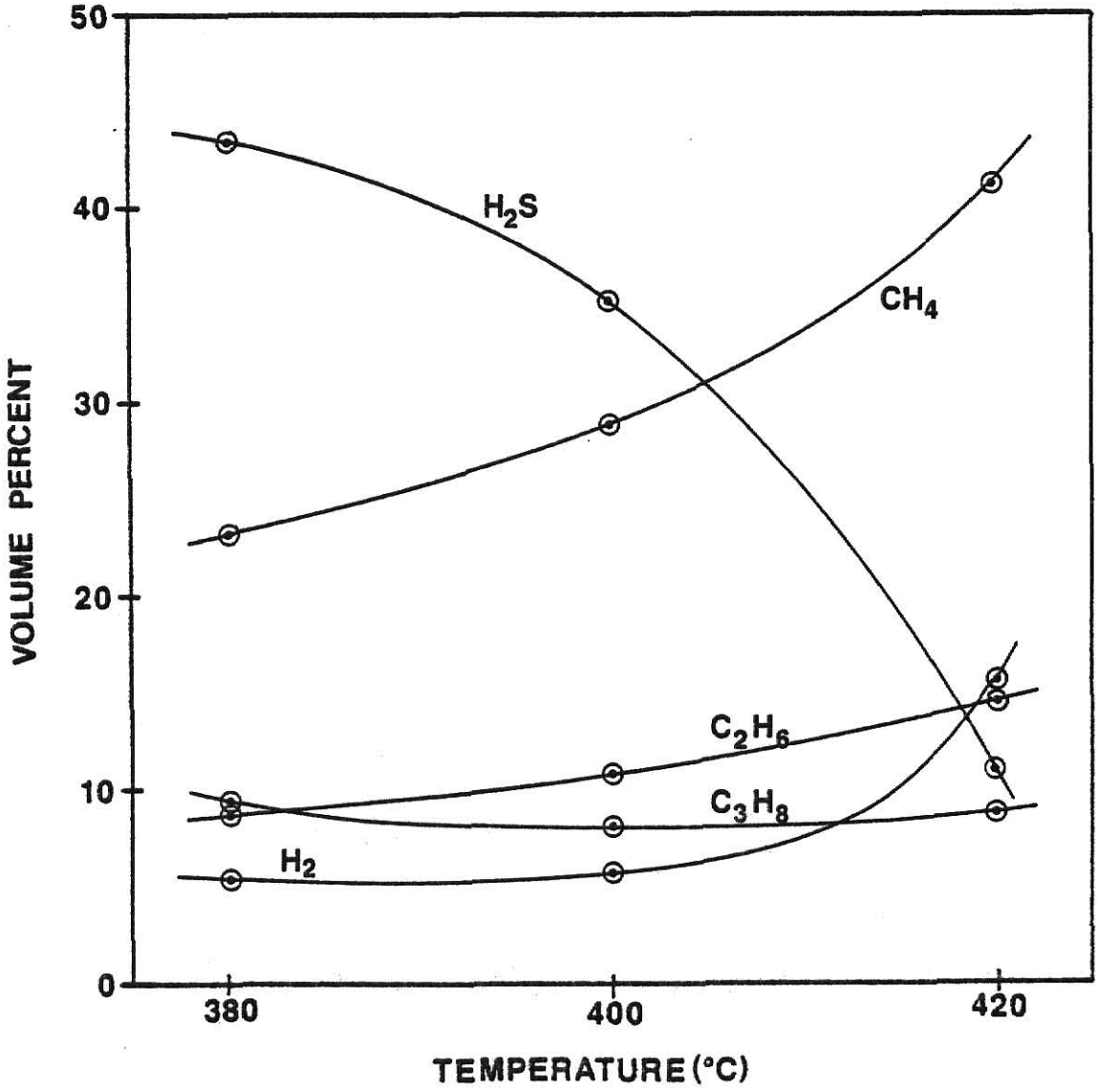


Figure 49. Major gas stream components:

380-(2:1)-60

400-(1:1)-30

420-(1.5:1)-60

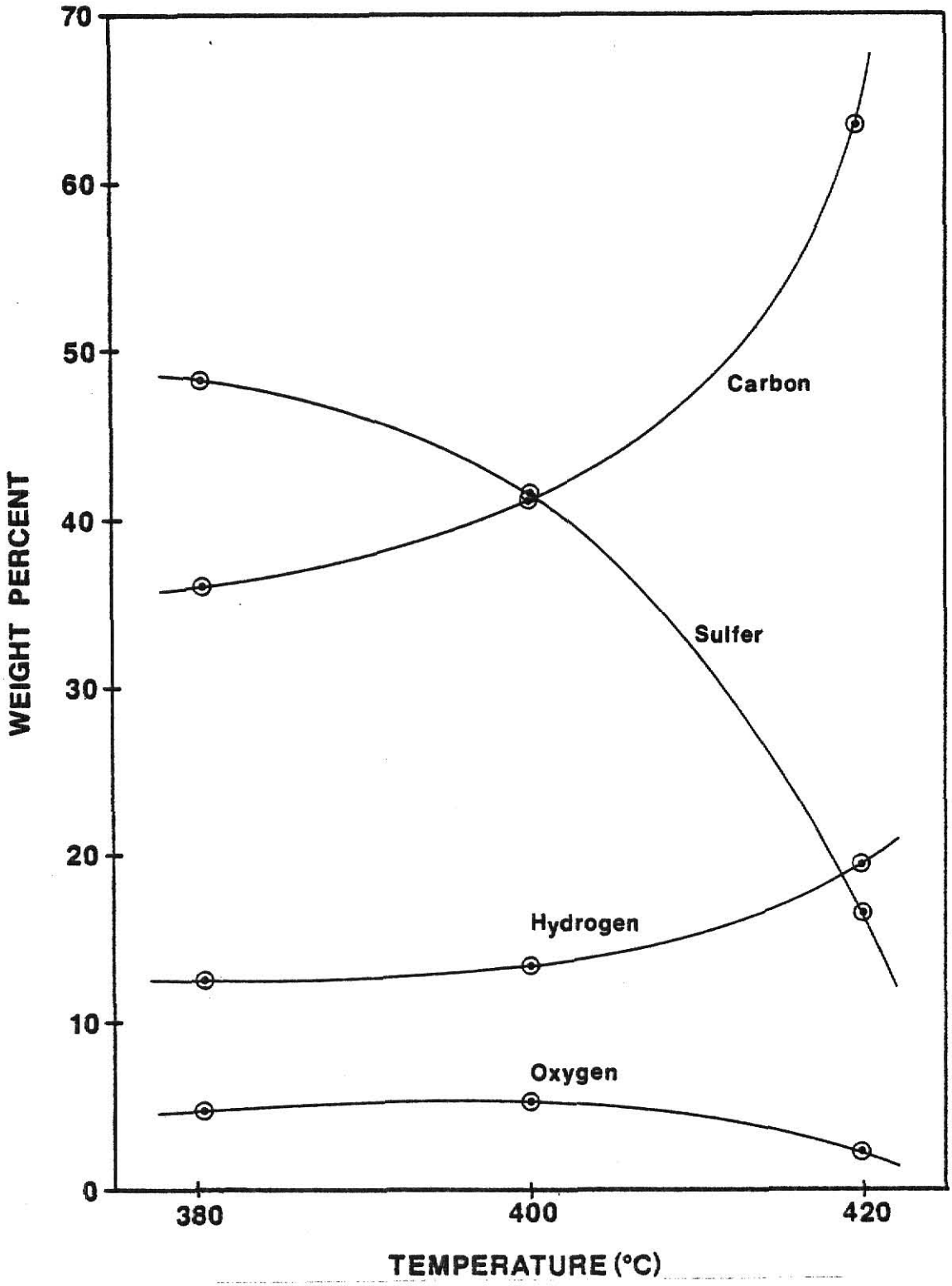


Figure 50. Gas stream elemental composition:

380-(2:1)-60

400-(1:1)-30

420-(1.5:1)-60

# APPENDIX 2

## EXPERIMENTAL RESULTS:

## SOLVOLYSIS LIQUEFACTION OF FOUR KANSAS COALS

This appendix contains the experimental results of the study presented in Chapter IV. Figures 1, 2, and 3 present the effect of ash content on the percent reduction of DAF solids. The effect of ash content on the product distribution is shown in Figures 4, 5, and 6. For a complete explanation of the plots and terms used in this appendix consult Chapter IV.

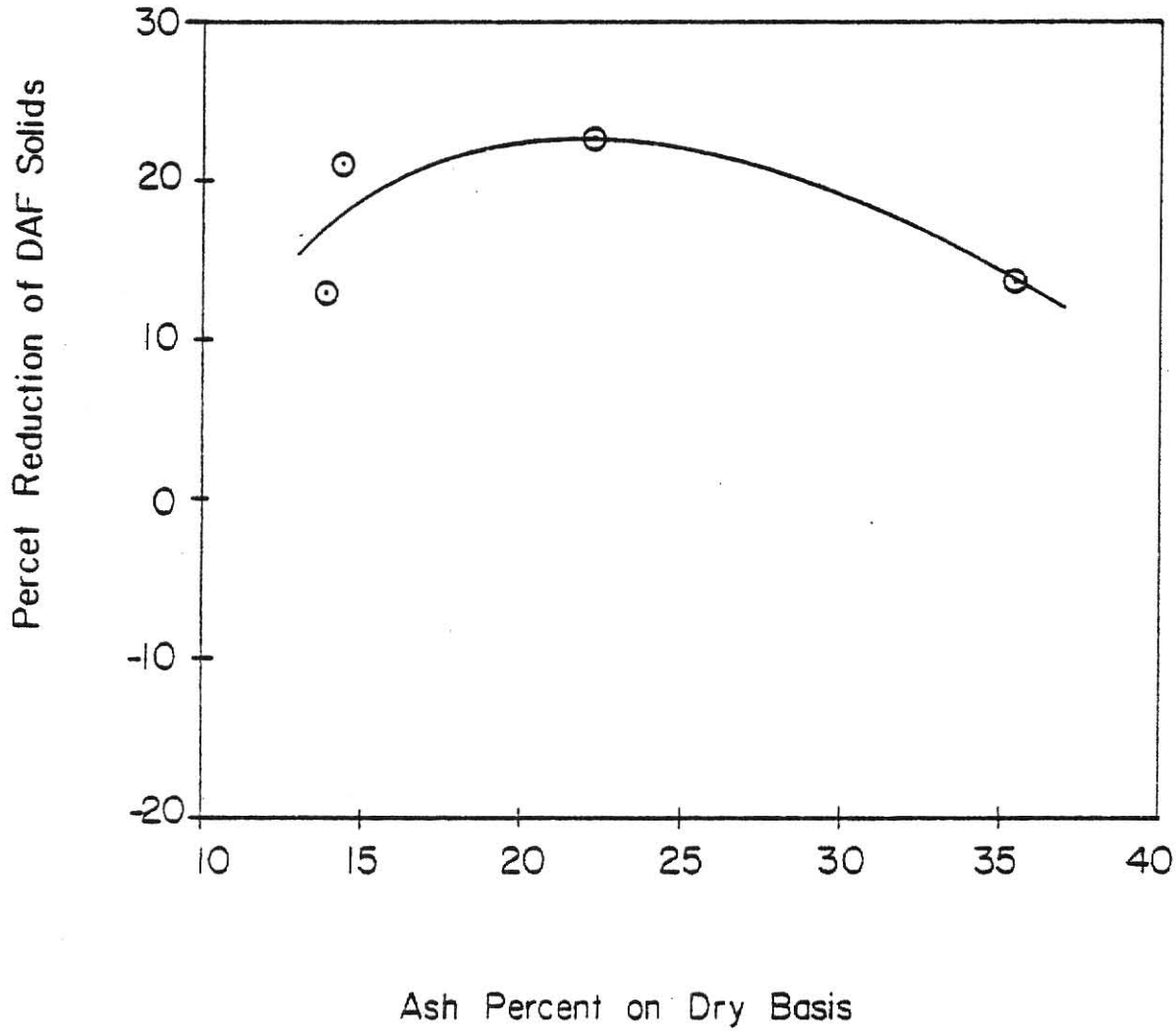


Figure 1. Effect of ash content on percent reduction of DAF solids:

Temperature = 380 $^{o}$C (653 K)
Time = 60 minutes
Solvent-to-Coal ratio = 2:1.

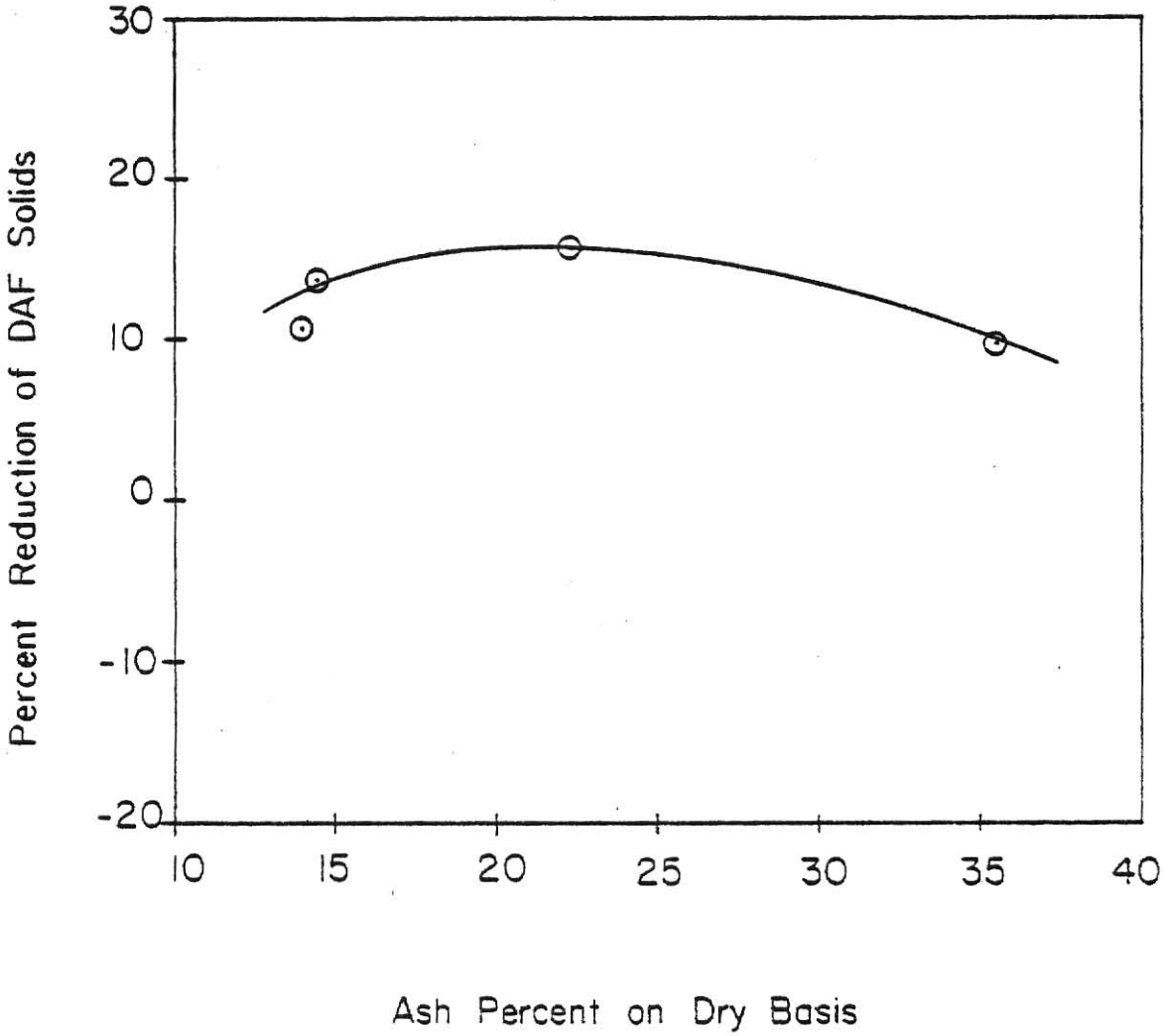


Figure 2. Effect of ash content on percent reduction of DAF solids:

Temperature = 400 °C (673 K)
Time = 30 minutes
Solvent-to-Coal ratio = 1:1.

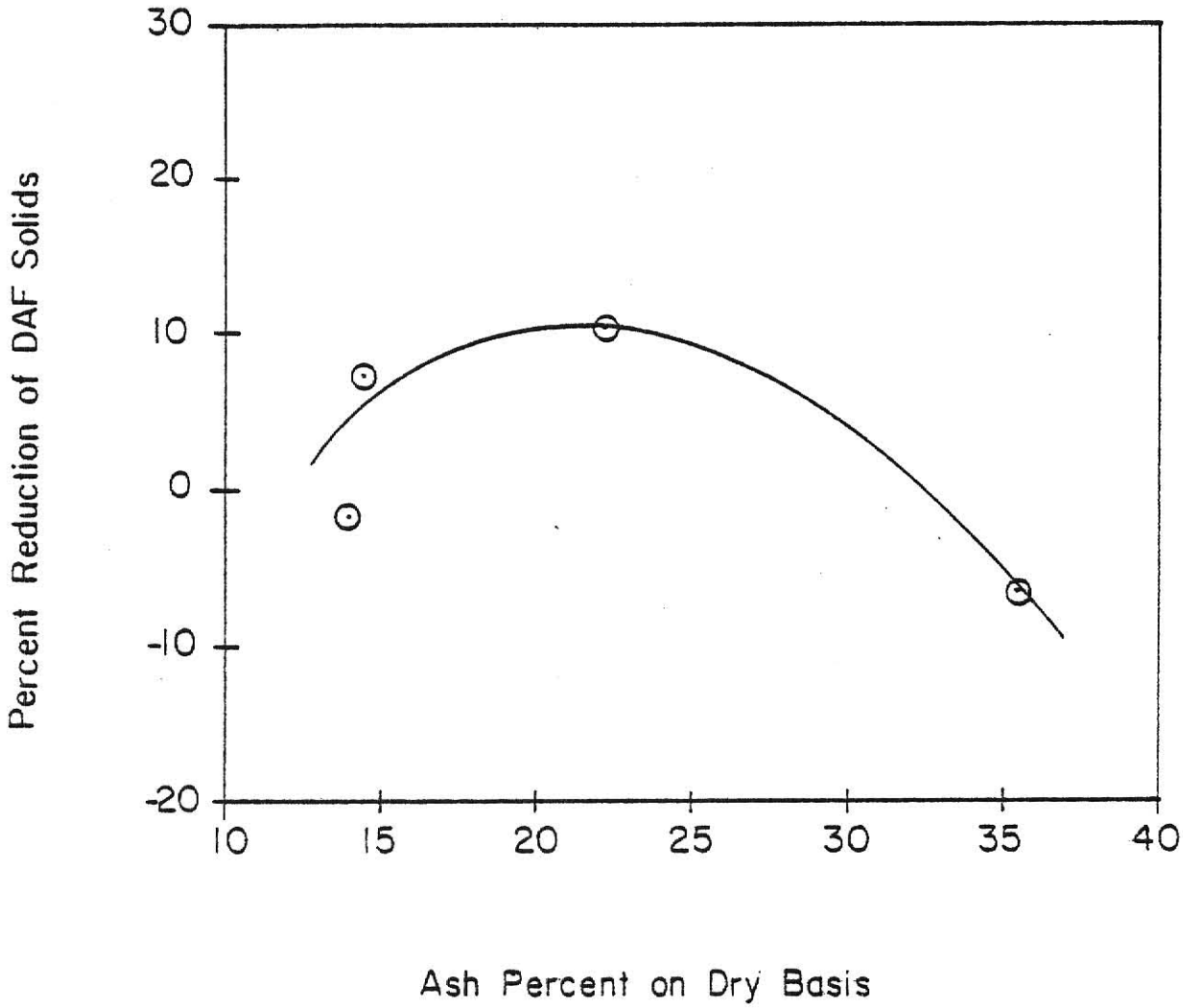


Figure 3. Effect of ash content on percent reduction of DAF solids:

Temperature = 420 °C (693 K)
Time = 30 minutes
Solvent-to-Coal ratio = 1.5:1.

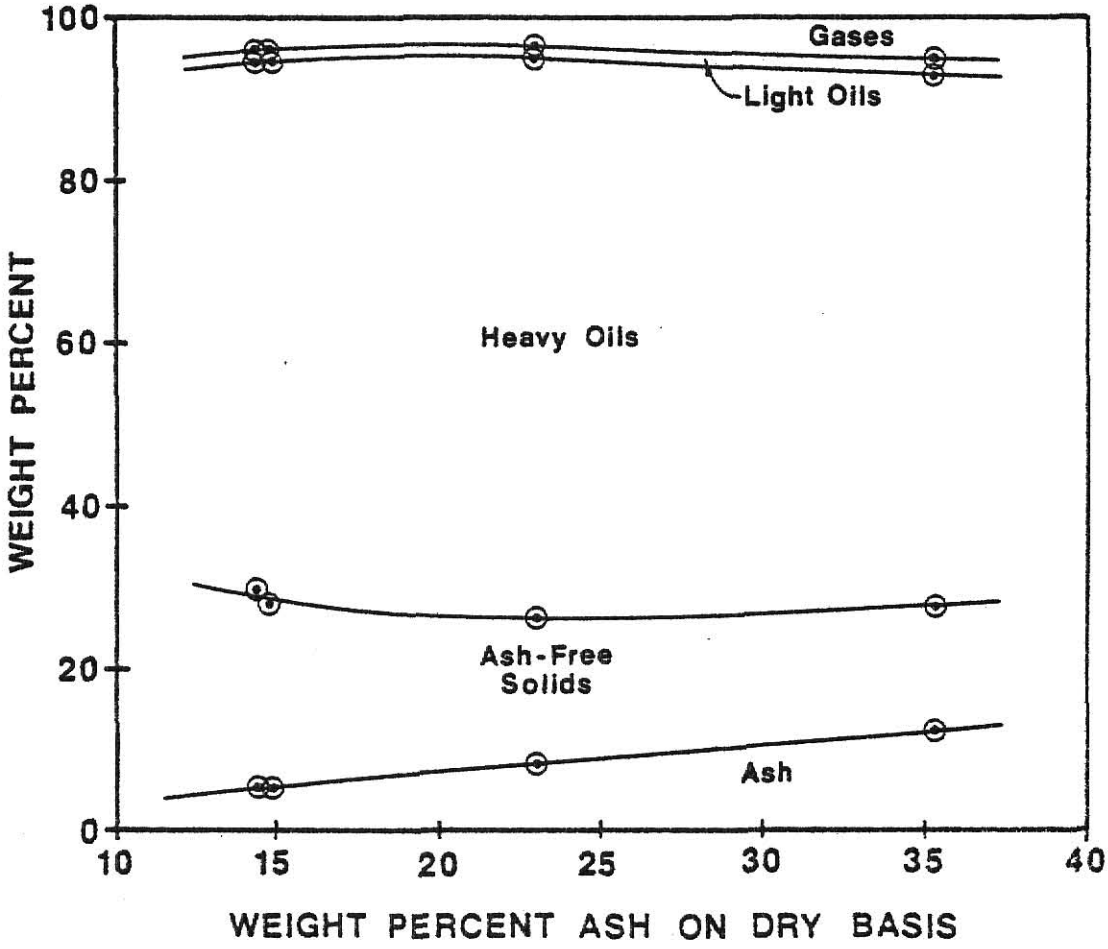


Figure 4. Effect of ash content on product distribution:

Temperature = 380 °C (653 K)
Time = 60 minutes
Solvent-to-Coal ratio = 2:1.

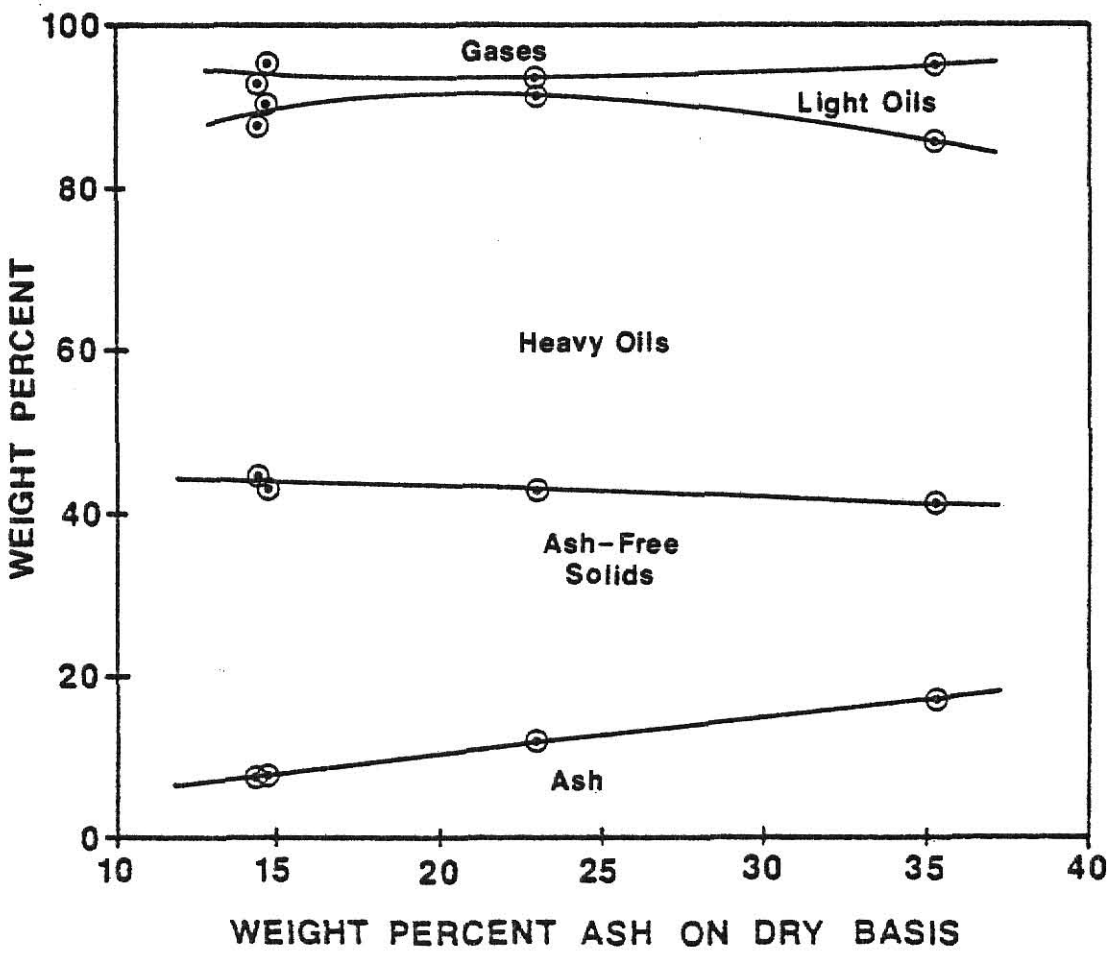


Figure 5. Effect of ash content on product distribution:

Temperature = 400 °C (673 K)
Time = 30 minutes
Solvent-to-Coal ratio = 1:1.

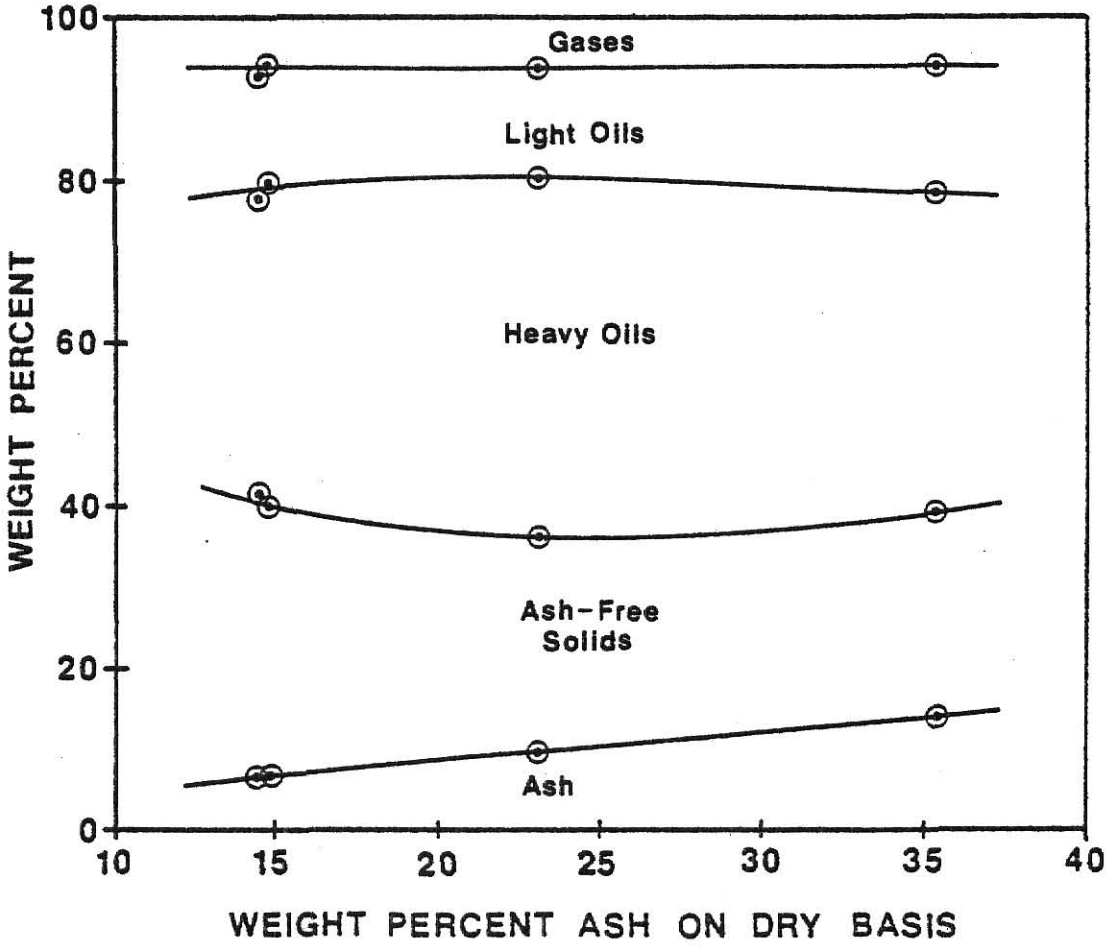


Figure 6. Effect of ash content on product distribution:

Temperature = 420 °C (693 K)
Time = 30 minutes
Solvent-to-Coal ratio = 1.5:1.

# SOLVOLYSIS LIQUEFACTION OF KANSAS COALS

by

WARREN MATTHEW EWERT

B. S., Kansas State University, 1978

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1980

Coal liquefaction fundamentals and results of the Exxon Donor Solvent, Solvent Refined Coal, and Kyushu-Koshi solvolysis liquefaction processes were reviewed. The results indicate that the Kyushu-Koshi process could be applied to several Kansas coals with the hopes of producing a low ash and sulfur heavy oil product.

An experimental study was undertaken to determine the variation of the product distribution and the percent reduction of dry ash-free (DAF) solids when Baxter coal was reacted with a refinery asphalt. Reaction temperature ranged from 360-400 $^{o}$C (633-693 K), reaction time varied from 0-90 minutes, and the solvent-to-coal weight ratio ranged from 1:1 to 5:1. A maximum percent reduction of DAF solids of 25% was observed at 400 $^{o}$C (673 K), with a solvent-to-coal ratio of 2:1, at a reaction time of 30 minutes. Extended reaction times and elevated temperatures resulted in coking of the asphaltenes due to the elimination of hydrogen-rich gases and light oils from the reaction system.

A second experimental study was made on four Kansas coals, Rowe, Bevier, Baxter, and Mulberry, which ranged in ash content from 14 to 36% on a dry basis. An increase in ash content resulted in a decreased percent reduction of DAF solids. The ash minerals are believed to promote catalytic dehydrogenation of the asphaltenes, thus producing coke rather than liquid heavy oils. Operation at pressures above one atmosphere would decrease the hydrogen loss in the form of gases and light oils and promote coal conversion in the Kyushu-Koshi process.