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(54) **Catalyst for coal liquefaction and process for liquefying coal using the same.**

(57) A catalyst for coal liquefaction consisting essentially of at least one substance which is able to be molten metal at 350 to 500°C in an atmosphere of hydrogen can give remarkably high conversion of coal when used as catalyst in a coal liquefaction reaction.

FIG. 1

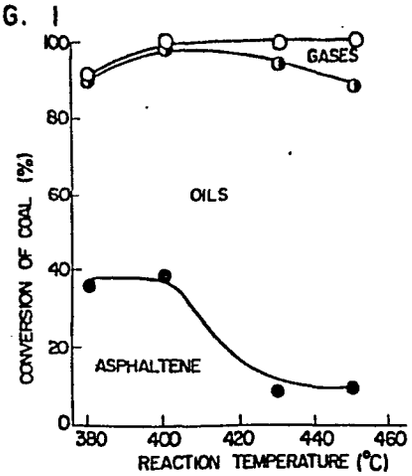
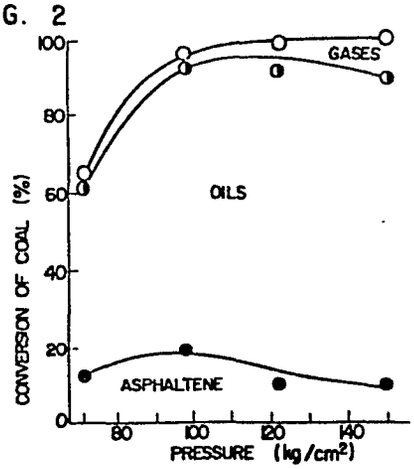


FIG. 2



EP 0 106 364 A2

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CATALYST FOR COAL LIQUEFACTION AND PROCESS FOR LIQUEFYING COAL USING THE SAME

This invention relates to a catalyst used in a process for liquefying coal by reacting coal with hydrogen and a process for liquefying coal using said catalyst.

Among processes for liquefying coal, there is a process in which coal is reacted with hydrogen in the presence of a catalyst at high temperatures under high pressure. Typical catalysts used in this coal liquefaction process are those carrying active components such as molybdenum, cobalt, nickel, etc., on a alumina carrier.

Recently, there was found a catalyst carrying a transition metal or a tin compound on a porous carrier containing magnesium silicate as a main component in place of the catalysts mentioned above (e.g., Japanese Patent Appln. Kokai (Laid-Open) No. 72079/81). According to said Japanese Patent Appln Kokai, the coal liquefaction reaction is carried out by subjecting coal in a solvent to hydrogenation treatment in the presence of a catalyst under a pressure of 50 to 500 kg/cm^2 at a temperature of 400 to 500°C. When molybdenum oxide and cobalt oxide carried on a magnesium silicate carrier is used as catalyst, the conversion of coal reaches 78.3% to 90.6%. But the conversion of coal is still insufficient and there are some problems due to the use of carrier for catalyst.

It is an object of this invention to provide a catalyst for coal liquefaction with a higher conversion of coal than the case of using the catalyst carrying an active component on a carrier containing magnesium silicate as a main component as mentioned above, and a process for liquefying coal by using said catalyst.

This invention provides a catalyst for coal liquefaction consisting essentially of at least one substance which is able to be molten metal at 350 to 500°C in an atmosphere of hydrogen.

This invention also provides a process for liquefying coal which comprises reacting coal in a solvent with hydrogen at a reaction temperature of 350 to 500°C under a reaction pressure of 50 to 700 kg/cm^2 in the presence of a catalyst consisting essentially of at least one substance which is able to be molten metal at 350 to 500°C in an atmosphere of hydrogen.

In the attached drawings, Fig. 1 is a graph showing a relationship between the conversion of coal and the reaction temperature, and Fig. 2 is a graph showing a relationship between the conversion of coal and the reaction pressure.

The catalyst of this invention is quite different from the known catalysts and the coal liquefaction process using the special catalyst of this invention is fundamentally different from the known coal liquefaction processes as will be explained below.

In the case of using the catalyst carrying an

active component such as nickel, molybdenum, cobalt, etc., on an alumina carrier and the catalyst carrying a transition metal or a tin compound on a porous carrier containing magnesium silicate as main component as mentioned above, the catalysts are present in the state of solid during the coal liquefaction reaction. Even in the case of carrying a tin compound on the porous magnesium silicate carrier, the tin compound is not melted substantially and remains in the state of solid. In such a case, since the tin compound is carried on micropores of the carrier, it is difficult to reduce the tin compound with hydrogen, and thus it is difficult to melt the tin compound.

In contrast, when the catalyst of this invention is used, the catalyst is subjected to reduction and becomes molten metal during the coal liquefaction reaction. The coal liquefaction reaction is proceeded in the presence of the molten metal thus produced as catalyst.

In the case of using the prior art catalysts mentioned above, that is, the catalysts being not melted during the coal liquefaction reaction, it is known that the coal liquefaction reaction proceeds as follows:

1st step: Coal is decomposed thermally to produce radicals.

2nd step: The radicals are stabilized by the hydrogen in the solvent.

3rd step: Low molecular compounds are produced by hydrogenation and hydrogenolysis.

The catalysts show activity only in the third step.

In contrast, when the catalyst of this invention is used, pyrolysis of coal in the first step can also be activated by the catalyst of this invention. This seems to be that the catalyst contacts with the surfaces of coal particles in molten state to show activity on the decomposition of coal. As a result, the conversion of coal can be raised.

As mentioned above, when the catalyst of this invention is used, the coal liquefaction steps are different from those when the prior art catalysts are used.

When the coal liquefaction is conducted by using the catalyst of this invention, the catalyst is present in the form of metal during the liquefaction raction. This is confirmed by X-ray diffraction. Further the presence of the catalyst in molten state is confirmed by differencial thermal analysis.

(1) Construction of Ctalyst

As the substance which is able to be molten metal at 350 to 500°C in an atmosphere of hydrogen, there can be used, for example, tin, zinc, bismuth, lead, gallium, cadmium, indium, selenium, tellurium, mercury and various compounds containing these metals, alone or as a mixture thereof.

In this invention, any substances can be used as catalyst, so long as said substances can be molten metal at 350 to 500°C in an atmosphere of hydrogen.

For example, there can be used metals as they are, metal oxides, metal chlorides, etc. Among them, the substances in the form of metal oxides are more preferable. The metal oxides are stable chemically and easy to handle.

Among the substances used as catalyst in this invention, those changing to molten metal during the coal liquefaction reaction and reacting with coal in such a state to produce organic compounds are preferable. Examples of such substances are tin, lead, zinc, cadmium, mercury and compounds containing these metals such as oxides, chlorides, etc. Among them, the use of tin, zinc, lead and their oxides is preferable from the viewpoint of easiness on handling.

When the substance which becomes molten metal during the metal liquefaction reaction and reacts with coal to produce organic compounds is used as catalyst according to this invention, the coal liquefaction reaction proceeds as follows:

1st step: Coal is decomposed thermally in the presence of molten metal catalyst to produce radicals.

2nd step: The radicals react with molten metal to produce organic compounds.

3rd step: The organic compounds are subjected to hydrogenolysis to produce oils or asphaltene and a metal. The metal produced by hydrogenolysis functions as catalyst again.

These reaction steps are quite different from those of using the prior art catalysts.

When the catalyst of this invention is used, the conversion of coal can be raised surprisingly highly. For example, when stannic oxide is used as catalyst, the coal conversion of as high as almost 100% can be obtained.

The shape of catalyst of this invention is not limitative, so long as the substance as catalyst is in the form of fine particles.

The smaller the particle size of the catalyst becomes, the better. When the catalyst particle size becomes smaller and smaller, mixing with coal becomes better and contact of the molten metal catalyst with coal can be bettered. In detail, the particle size of catalyst is preferably 1 mm or less, more preferably 0.1 mm or less. For example, when metallic tin is used as catalyst and the reaction is carried out at 450°C under a pressure of 150 kg/cm^2, almost 100% of the coal oonversion is obtained in the case of the particle size of 0.1 mm, and about 95% of the coal conversion is obtained in the case of the particle size of 2 mm.

Further, the catalyst of this invention does not use a carrier. When a carrier is used, most portions of a catalyst do not change to molten metal at the time of coal liquefaction reaction and remains in the form of solid, which results in lowering the conversion of coal.

(2) Amount of Ctalyst to be used

The conversion of coal also changes depending on the using amount of catalyst. The catalyst of this

invention in an amount of 0.01% by weight based on the weight of coal shows a sufficient effect. The conversion of coal increases with an increase of the amount of catalyst used until 1% by weight of the catalyst based on the weight of coal and maintains its high value even if the catalyst amount is more than 1% by weight. In other words, the effect of catalyst for coal conversion is the best when the using amount of catalyst becomes 1% by weight based on the weight of coal. Therefore, the catalyst is used particularly preferably in an amount of 1% by weight or more based on the weight of coal. When the catalyst is used in an amount of 0.2% by weight or more based on the weight of coal, remarkably high conversion of coal can be obtained.

On the other hand, the use of too much amount of catalyst is useless and not preferable from an economical point of view. It is sufficient to use 10% by weight or less, particularly 5% by weight or less of the catalyst of this invention based on the weight of coal.

(3) Preparation of Catalyst.

The catalyst of this invention can be prepared by various processes.

As processes for preparing tin oxides, i.e., stannic oxide and stannous oxide, there can be applied, for example, a process wherein metallic tin is reacted with an acid to synthesize stannic acid, followed by calcination and pulverization; a process wherein a salt of tin is hydrolyzed, followed by calcination and

pulverization; a process wherein metallic tin is calcined in air and pulverized; a process wherein a salt of tin or an organotin compound is subjected to pyrolysis and pulverized; and the like.

As processes for preparing zinc oxide, there can be applied, for example, a process wherein an alkali is added to a water-sluble zinc salt to precipitate a hydroxide, followed by calcination and pulverization; a process wherein metallic zinc is calcined in air for oxidation, followed by pulverization; a process wherein an organozinc compound is subjected to pyrolysis, followed by pulverization; and the like.

Among the processes for preparing tin oxides, the process wherein metallic tin is reacted with an acid to synthesize stannic acid, followed by calcination and pulverization is most preferable. Among the processes for preparing zinc oxide, the process wherein an alkali is added to a water-soluble zinc salt to precipitate a hydroxide, followed by calcination and pulverization i most preferable. When the tin oxides or zinc oxide prepared by the most preferable processes as mentioned above is used as catalyst for coal liquefaction, the highest conversion of coal can be obtained compared with the cases of using tin oxides or zinc oxide prepared by other processes.

(4) Coal Liquefaction Process

In order to conduct the coal liquefaction reaction, it is necessary to admix coal, a solvent and the

catalyst of this invention and to react the coal with hydrogen at a prescribed temperature under a prescribed pressure in a reactor.

After the reaction, the resulting products are separated into gases, oils and solids (residue after liquefaction). Those which are retained as solids are ashes such as alumina, silica, etc., contained in coal, unreacted coal and the catalyst. When the prior art catalysts are used, since a considerably large amount of unreacted coal is retained, the recovery of the catalyst is very difficult and the residue after liquefaction is disposed. In contrast, in the present invention, particularly when the substance which becomes molten metal at the time of liquefaction reaction and reacts with coal to produce organic compounds is used as catalyst, the conversion of coal becomes remarkably high and almost no unreacted coal is retained, so that the recovery of the catalyst is easy. Therefore, it is possible to recover the catalyst and to use it again. Further, when the amount of ashes in the residue after liquefaction is small, the solid can be used again as catalyst as it is. In the case of using the solid as it is as catalyst again, it is possible to use again a part of the solid as it is and to recover the catalyst from the remaining solids and to use the recovered catalyst by mixing with the part of the solid mentioned above in order to prevent the increase of ash content.

The reaction temperature is usually 350 to 500°C,

preferably 400 to 480°C. If the reaction temperature is higher than 500°C, the amount of gases increases too much and the amount of oils becomes too small. If the reaction temperature is lower than 350°C, there hardly takes place the reaction between coal and hydrogen and the liquefaction reaction does not proceed.

Effects of the reaction temperature on the conversion of coal is explained referring to Fig. 1. Fig. 1 is a graph showing a relationship between the reaction temperature and the conversion of coal when the coal liquefaction reaction is conducted by using stannic oxide having a particle size of 74 μm as catalyst in an amount of 5% by weight based on the weight of coal under a pressure of 150 kg/cm^2 for 30 minutes. It is clear that when the reaction temperature is 400°C or higher, the producing amount of oils (the area between the line of - ○ - ○ - and the line of - ● - ● -) increases.

The reaction pressure is usually 50 - 700 Kg/cm^2, preferably 100 to 200 Kg/cm^2.

The reaction between coal and hydrogen does not proceed under an atmospheric pressure. In order to proceed the reaction, at least the pressure of 50 kg/cm^2 is necessary. The higher the reaction pressure becomes, the higher the conversion of coal becomes. But when the pressure becomes 200 kg/cm^2 or more, the conversion of coal hardly changes. The maximum pressure should be determined considering the material of the reactor and resistance to pressure. The pressure of 700 kg/cm^2 or

less is sufficient for the coal liquefaction reaction.

Effects of the reaction pressure on the conversion of coal is explained referring to Fig. 2. Fig. 2 is a graph showing a relationship between the reaction pressure and the conversion of coal when the coal liquefaction reaction is conducted by using stannic oxide having a particle size of 74 μm as catalyst in an amount of 5% by weight based on the weight of coal at a temperature of 450°C for 30 minutes. The higher the pressure becomes, the higher the conversion of coal becomes. When the pressure is 100 kg/cm^2 or more, the yield of oils clearly increases.

The coal is preferably used in fine particles by pulverizing well. The finer the particles of coal becomes, the easier the liquefaction by the reaction with hydrogen becomes. It is preferable to make the particle size of coal 0.5 mm or less.

As the solvent, there can be used anthracene oil, tetralin, creosote oil or liquiefied oils by the coal liquefaction reaction. It is most convenient to use the liquefied oils produced by the coal liquefaction reaction as a part of the solvent. The amount of the solvent changes depending on the viscosity of the slurry. The more the amount of solvent becomes, the smaller the treating amount of coal becomes. When the amount of the solvent used is small, the viscosity of the resulting slurry becomes lower and the feeding of coal to the reactor becomes difficult. It is preferable to use the

solvent in an amount of 1 to 3 times as large as that of the weight of the coal.

This invention is illustrated by way of the following Examples.

Example 1

The coal liquefaction was conducted by using stannic oxide (SnO_2) as catalyst.

The stannic oxide catalyst was prepared by reacting metallic tin with nitric acid, kneading the reaction product, drying, calcinating at 450°C for 3 hours, followed by pulverization. The particle size of the catalyst after the pulverization was 74 μm or less.

The thus produced stannic oxide in an amount of 1.0 g was mixed with 20 g of Taiheiyo coal (produced in Japan) and 40 g of creosote oil and placed in an autoclave with stirring. The Taiheiyo coal had been crushed into a particle size of 0.1 to 0.4 mm. The amount f the catalyst used was 5% by weight based on the weight of the coal.

After introducing hydrogen into the autoclave, the temperature was raised to 450°C and the reaction was conducted under a pressure of 150 kg/cm^2 for 30 minutes.

The reaction product was taken out of the autoclave and extracted with n-hexane to extract the oil component by a Soxhlet's extractor. The residue was extracted with toluene to separate asphaltene.

The conversion of coal was obtained by a conventionally used dry ash free base (the calculation

being conducted by withdrawing the amounts of ashes and water). The conversion of coal, yields of oils, gases, asphaltene in the products were as follows:

Conversion of coal	100%
Yield of oils	73.1%
Yield of asphaltene	12.7%
Yield of gases	14.2%

Example 2

The coal liquefaction was conducted by using zinc oxide (ZnO) as catalyst.

The zinc oxide catalyst was prepared by neutralizing zinc nitrate with ammonia water, filtering a precipitate produced, drying, calcinating at 450°C for 3 hours, followed by pulverization. The particle size of catalyst after pulverization was 74 μm or less.

Using the thus prepared catalyst, the coal liquefaction was conducted in the same manner as described in Example 1.

The conversion of coal and yields of the products were as follows:

Conversion of coal	99.1%
Yield of oils	74.3%
Yield of asphaltene	15.0%
Yield of gases	10.7%

Example 3

The coal liquefaction was conducted by using

lead oxide (PbO) as catalyst.

The lead oxide catalyst was prepared by heating lead acetate in air at 450°C for 2 hours for pyrolysis to give lead oxide, followed by pulverization to give a particle size of 74 μm or less.

Using the thus prepared catalyst, the coal liquefaction was conducted in the same manner as described in Example 1.

The conversion of coal and yields of the products were as follows:

Conversion of coal	99.7%
Yield of oils	76.9%
Yield of asphaltene	12.4%
Yield of gases	10.7%

Example 4

The coal liquefaction was conducted by using bismuth oxide (Bi_2O_3) as catalyst.

The bismuth oxide catalyst was prepared by heating bismuth nitrate in air at 450°C for 2 hours to conduct pyrolysis, followed by pulverization to give a particle size of 74 μm or less.

Using the thus prepared catalyst, the coal liquefaction was conducted in the same manner as described in Example 1.

The conversion of coal and yields of the products were as follows:

Conversion of coal	92.1%
Yield of oils	59.7%
Yield of asphaltene	31.5%
Yield of gases	8.8%

Example 5

The coal liquefaction was conducted by using gallium oxide (Ga_2O_3) as catalyst.

The gallium oxide catalyst was prepared by heating gallium nitrate in air at 450°C for 2 hours to conduct pyrolysis, followed by pulverization to give a particle size of 74 μm or less.

Using the thus prepared catalyst, the coal liquefaction was conducted in the same manner as described in Example 1.

The conversion of coal and yields of the products were as follows:

Conversion of coal	95.4%
Yield of oils	71.6%
Yield of asphaltene	16.9%
Yield of gases	11.5%

Comparative Example 1

The coal liquefaction was conducted by using a catalyst carrying 5% by weight of stannic oxide on an alumina carrier.

The catalyst was prepared by kneading an aluminum hydroxide slurry obtained by hydrolysis of aluminum

isopropoxide with stannic acid slurry, drying, calcining at 450°C for 3 hours, followed by pulverization.

Using the thus prepared catalyst, the coal liquefaction was conducted in the same manner as described in Example 1.

The conversion of coal and yields of the products were as follows:

Conversion of coal	76.5%
Yields of oils	53.6%
Yields of asphaltene	44.0%
Yields of gases	2.4%

Comparative Example 2

The coal liquefaction was conducted by using a catalyst carrying molybdenum oxide (MoO_3) and nickel oxide (NiO) on an alumina (Al_2O_3) carrier.

The catalyst can be obtained commercially in Japan and has a particle size of 74 μm or less.

Using the this catalyst, the coal liquefaction was conducted in the same manner as described in Example 1.

The conversion of coal and yields of the products were as follows:

Conversion of coal	71.8%
Yield of oils	62.7%
Yield of asphaltene	11.9%
Yield of gases	25.4%

As is clear from the above descriptions, when the coal liquefaction reaction is conducted by using the catalyst of this invention, the conversion of coal can be raised to a remarkable height. Particularly when there is used a catalyst consisting essentially of a substance such as stannic oxide or zinc oxide which is reduced to molten metal at the time of liquefaction reaction, followed by reaction with coal, the conversion of coal can be raised remarkably high.

WHAT IS CLAIMED IS:

1. A catalyst for coal liquefaction consisting essentially of at least one substance which is able to be molten metal at 350 to 500°C in an atmosphere of hydrogen.

2. A catalyst according to Claim 1, wherein the substance is a metal oxide.

3. A catalyst according to Claim 1, wherein the substance is able to be molten metal and is able to produce organic compounds by a reaction with coal.

4. A catalyst according to Claim 2, wherein the metal oxide is bismuth oxide.

5. A catalyst according to Claim 2, wherein the metal oxide is gallium oxide.

6. A catalyst according to Claim 2, wherein the metal oxide is stannic oxide and/or stannous oxide.

7. A catalyst according to Claim 2, wherein the metal oxide is zinc oxide.

8. A process for liquefying coal which comprises reacting coal in a solvent with hydrogen at a reaction temperature of 350 to 500°C under a reaction pressure of 50 to 700 kg/cm^2 in the presence of a catalyst consisting essentially of at least one substance which is able to be molten metal at 350 to 500°C in an atmosphere of hydrogen.

9. A process according to Claim 8, wherein the substance is used in an amount of 0.01 to 10% by weight based on the weight of coal.

10. A process according to Claim 8, wherein the substance has a particle size of 1 mm or less.

11. A process according to Claim 8, wherein the substance is a metal oxide.

12. A process according to Claim 11, wherein the metal oxide is bismuth oxide.

13. A process according to Claim 11, wherein the metal oxide is gallium oxide.

14. A process according to Claim 11, wherein the substance is able to be molten metal and is able to produce organic compounds by a reaction with coal.

15. A process according to Claim 11, wherein the metal oxide is stannic oxide and/or stannous oxide.

16. A process according to Claim 8, wherein the reaction temperature is 400 to 480°C.

17. A process according to Claim 8, wherein the reaction pressure is 100 to 200 kg/cm^2.

18. A process according to Claim 11, wherein the metal oxide is zinc oxide.

19. A process for liquefying coal which comprises reacting coal in a solvent with hydrogen at a reaction temperature of 350 to 500°C under a reaction pressure of 50 to 700 kg/cm^2 in the presence of a catalyst consisting essentially of at least one substance which is able to be molten metal at 350 to 500°C in an atmosphere of hydrogen, and taking out a part of residue after liquefaction to use again as catalyst or recovering the catalyst from a residue after liquefaction to use again

as catalyst.

20. A process according to Claim 19, wherein the substance is able to be molten metal and is able to produce organic compounds by a reaction with coal.

21. A process according to Claim 20, wherein the substance is stannic oxide and/or stannous oxide.

FIG. 1

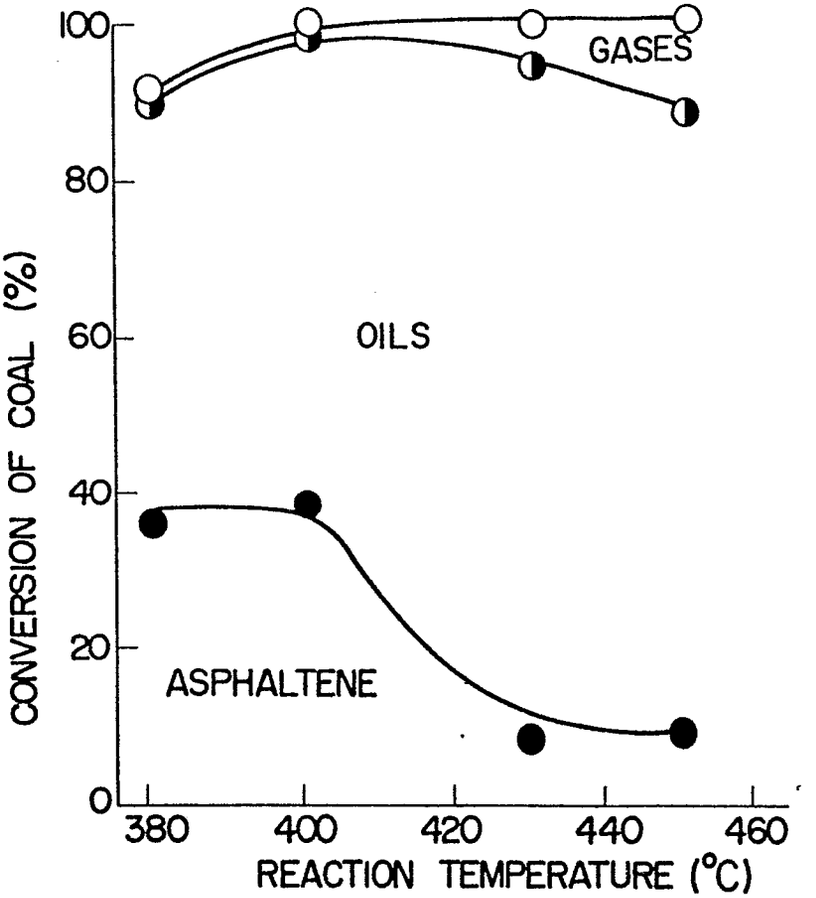
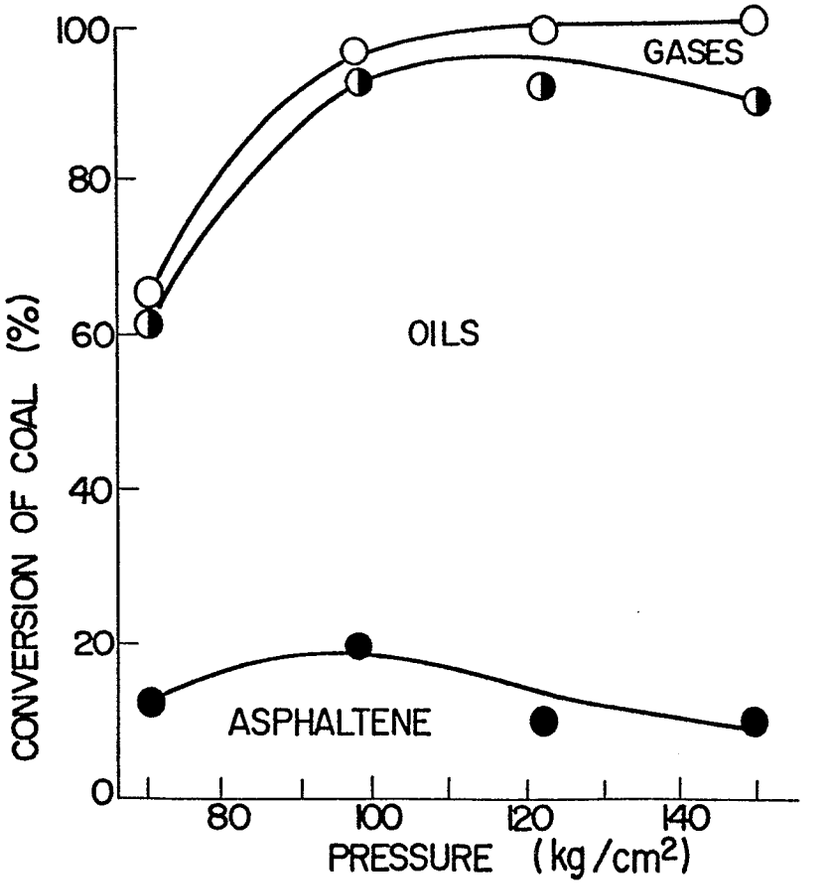

100
80
60
40
20
0
GASES
OILS
ASPHALTENE
CONVERSION OF COAL (%)
380
400
420
440
460
REACTION TEMPERATURE (°C)

FIG. 2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80
60
40
20
0
GASES
OILS
ASPHALTENE
CONVERSION OF COAL (%)
80
100
120
140
PRESSURE (kg/cm²)