SHELL COAL GASIFICATION PROCESS

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Summary

The entrained Shell Coal Gasification Process operating under slagging conditions and elevated pressure features:

- practically complete gasification of most coals;
- high reactor throughput;
- high thermal efficiency and efficient heat recovery;
- production of a clean gas without byproducts;
- environmental advantages.

The present paper highlights the environmental aspects of the process:

- gas treating;
- methods to maximize slag production;
- slag leaching;
- uses for waste material;
- water treating.

There are numerous possible future applications for this process. The gas produced (93-98%v hydrogen and carbon monoxide) is suitable for the manufacture of hydrogen or reducing gas and, with further processing, substitute natural gas (SNG). Moreover, the gas can be used for the synthesis of ammonia, methanol and liquid hydrocarbons.

Another possible application of this process is as an integral part of a combined-cycle power station featuring both gas and steam turbines. Such integration of a Shell coal gasifier with a combined-cycle power station will allow for electricity generation at 42-45% efficiency for a wide range of feed coals.

The development program includes the operation of a 150 t/d gasifier at Deutsche Shell's Harburg refinery since November 1978 and of a 6 t/d process development unit at Royal Dutch Shell's Amsterdam laboratories from December 1976 onwards. The next step will be the construction and operation of 1000-2000 t/d prototype plants which are scheduled for commissioning in 1985/86. Towards the end of the eighties, large

commercial units with 2500 t/d gasifiers are contemplated. The economy, especially of these large scale units, is very competitive.

Development of the Shell Coal Gasification Process (SCGP)

Shell Internationale Petroleum Maatschaapij B.V., The Hague, have been working since 1973 on the development of a high-pressure slagging coal gasification process using their experience and know-how on the high pressure oil gasification process, the so-called Shell Gasification Process. A process development unit (PDU) of 6 tons per day intake capacity has been in operation at Shell's Amsterdam Laboratories since December 1976. As part of this development, Deutsche Shell AG decided to set up an experimental plant employing this process. This has resulted in a 150 t/d pilot plant which was completed in November 1978 (see Figure 1). The plant has, so far, gasified coal during almost 2000 hours with a longest run of 240 hours.

Based on the experience with the experimental units, designs are being made for two 1000-2000 t/d prototype units, one in Moerdijk, Holland, and one in Wilhelmshaven, Federal Republic of Germany, which are scheduled for commissioning in 1985/86. The capacities of subsequent fully commercial units will be increased stepwise to about 2500 t/d per gasifier towards the end of the eighties.

The Process

The process is based on the principle of entrained bed gasification at elevated pressure under slagging conditions (e.g. at temperatures sufficiently high to ensure that the ash is in the molten state). The main technical features of the process are described below.

Process Features

Complete Conversion of Most Coals. The process is suitable for the complete gasification of a wide variety of solid fuels, such as almost all types of coal and petroleum coke. The process is expected to be able to gasify fuels with high ash (up to 40%) and sulfur (up to 8%w) without difficulty. Even a high water content in the coal does not pose a technical problem. However, on economic grounds, particularly with a view to reducing the oxygen requirement, and improving the quality of the gas, the coal is in most cases dried to a moisture content of 1-6%w.

As the process in any case requires a solid fuel to be in dust form for gasification, the entire output of a mine, including fines, is acceptable as feed. Unlike most other gasification processes, in SCGP there is, in principle, practically no limitation on the coal as to caking properties, coal rank or coal integrity. With hard coal a conversion of 99% can be reached while producing a gas with only 1%v CO_2.

We also expect to be able to gasify vacuum residues of direct coal liquefaction plants and other hydrocarbon liquids in an SCGP type reactor.

An advantage of such a process over the Shell Gasification Process for oil is that liquids containing unconverted coal and a high percentage of ash can be gasified.

Large Unit Capacity. Both the high temperatures of above 1400°C and the high pressures (generally above 20 bar) are responsible for the high capacities attainable. Short-term targets are 50-100 t/hr of coal per reactor, corresponding to 2.4-4.8 million Nm^3/day of raw gas.

Depending on the application, the optimum pressure level can be selected. Apart from the beneficial effect of the elevated pressure on reactor capacity, there are spin-offs in terms of increased heat transfer rates in the waste heat boiler, more economic gas treating and a reduction in gas compression costs.

High Thermal Efficiency and Efficient Heat Recovery. The chemically bound heat in the gas produced with oxygen gasification is equivalent to about 79 to 82% of the chemically bound heat contained in the dried coal feed. The recovery of the sensible heat from the hot gases leaving the reactor accounts for another 12-15% of the heat content of the coal feed. The steam produced by this cooling is generally sufficient to drive the compressors of the oxygen plant.

Heat losses to atmosphere are reduced to a minimum. The combined operation of reactor cooling system and waste heat boiler results in an efficient heat recovery by the production of superheated high-pressure steam (typically 520°C, 100 bar).

Clean Gas Production without Formation of Byproducts. The operation at very high temperature ensures the formation of a high quality synthesis gas essentially consisting of hydrogen and carbon monoxide (93-98%v for oxygen gasification). Tars, phenols and hydrocarbons heavier than C_1 are absent; as a rule methane concentrations in the gas do not exceed 0.2%v.

Sulfur components in the gas are H_2S and COS whereas nitrogen is present as N_2, HCN and NH_3. All sulfur components are eventually converted into elemental sulfur whereas HCN is mainly converted to NH_3 and partially to water-soluble degradable cyanide derivatives. The process line-up and the commercially proven processes used to accomplish these conversions are discussed in the section on "Removal of Nitrogen and Sulfur Compounds."

Environmental Acceptability. The Shell Coal Gasification Process offers important environmental advantages. The observations and conclusions presented here are based on pilot testing of specific coals most of which are European. We believe American coals, too, can be gasified with acceptable environmental impacts by employing appropriate control technologies.

The only byproducts from the process are elemental sulfur, CO_2, the unavoidable ash from the coal, ammonia (if desired as a product), a small treated wastewater stream and sludge from flocculation/sedimentation/biotreatment.

Ash is partially converted into slag which is essentially non-leachable for most coals. Depending on the ash composition, it may be necessary to run out part of the ash as fly slag which may have to be processed further to render it environmentally acceptable. This is discussed in "Ash and Slag Removal" below.

The processing of waste water is discussed in "Waste Water Treatment."

Simplified Flow Scheme (Figure 2)

In a coal mill, coal is ground and dried to specification and subsequently pneumatically transported to the atmospheric hoppers. To transport the coal from the cyclone hopper to the pressurized feed hopper, a fully automatic lock hopper system is used. The pneumatic transport of the coal from the feed hoppers to the burners is accomplished with nitrogen or syngas, depending on whether the product gas is used as fuel gas or syngas.

For good control of the process, it is mandatory to be able to measure accurately the coal, oxygen and steam flow to the burners. The success of the pneumatic feed system has been made possible by the development of an accurate and dependable coal flow meter.

The reactor is equipped with one or two diametrically opposed burner pairs and consists essentially of a pressure shell which is protected from the hot gases by a tube wall in which saturated steam of 100 bar is raised.

The tube wall is in turn protected by a thin layer of a refractory material.

The slag which leaves the reactor via a hole in the bottom is quenched in water and then lock-hoppered out to atmospheric pressure.

The gases leaving the reactor at about 1500°C and 30 bar are quenched with solids free recycled synthesis gas of 100°C to 800-900°C in order to solidify the entrained slag particles before they enter the waste heat boiler. The gases leave the waste heat boiler at a temperature of 320°C. In the waste heat boiler superheated steam of 520°C and 100 bar is raised.

The bulk of the solids in the gas are removed in cyclone(s) which are located downstream of the waste heat boiler. The remainder of the solids is washed out with water in a series of scrubbers and separators after the gas has been further cooled in an economizer. The gas leaving the scrubbers has a solids content of 1 mg/Nm^3 and a temperature of 40-80°C.

Part or all of the solids in the circulating water are concentrated in a slurry which will be reinjected upstream of the cyclone. The water will then evaporate and most if not all solids leaving the waste heat boiler will eventually be separated in the cyclone, thus minimizing the need for filtration of ash from a waste water bleed stream. This system has already run very successfully both in our 6 t/d pilot plant at our Amsterdam Laboratories and in the 150 t/d unit in Harburg.

Blast Requirements, Product Gas and Thermal Efficiency

Oxygen and steam consumptions are dependent on the coal feedstock quality. An oxygen demand of 0.9-1.0 ton per ton of moisture and ash-free coal is fairly typical of hard coals; for low-rank coals, a figure of 0.8 tons of oxygen per ton of MAF (Moisture and Ash Free) coal is more representative. The process steam requirement is very low and, in fact, is almost zero for some brown coals. For hard coal, it is of the order of 8% on MAF coal.

The raw gas production is about 2000 m^3 per ton for a good quality bituminous coal. The gas is relatively rich in carbon monoxide and the CO/H_2 ratio, on a volume basis, is typically between 1.8 and 2.2 for the preferred operation at minimum steam dosage.

The heat content of the gas is of the order of 11.3 MJ/Nm^3 (300 BTU/scf). The thermal efficiency, of the gasification proper is about 82% for oxygen/steam gasificiation. Apart from this percentage of the total heat in the coal which is recovered as chemical heat in the gas, about 15% of the heat in the coal to the gasifier becomes available for steam raising in the waste heat boiler via the sensible heat in the gas.

The total heat content of synthesis gas and steam represents approximately 94-97% of the heat content of the coal feed. It is, however, more realistic to consider the overall thermal efficiency taking into account the energy consumption of oxygen plant, coal mill and dryer, coal gasifier and auxilliary equipment. This overall thermal efficiency calculated on a lower heating value basis, corresponds to approximately 78% for a 12% ash, 7% moisture hard coal.

Coal Quality

To demonstrate the versatility of the Shell Coal Gasification Process vis-a-vis feed coal quality, the thermal efficiency has been calculated for a range of coals, viz:

- bituminous coal with moderate ash and moisture content (Auguste Victoria (German) and Illinois No. 6)
- sub-bituminous coal (Wyodak);
- coal liquefaction vacuum bottoms;
- brown coal, high moisture, low ash (German brown coal).

These feedstocks cover a fairly wide range of ash and moisture contents (Table I). The calorific values, correspondingly, range from 10 to 29 GJ/t as received coal.

The data presented in Table II are indicative of the oxygen and steam consumptions, and of the overall thermal efficiencies for the coal feedstocks specified. Assuming a constant production of synthesis gas ($CO + H_2$), it is evident that the amount of coal to be processed increases as the rank, and correspondingly the heating value, of the coal goes down and as moisture and ash contents go up. Variations in oxygen demand are generally well below 10% for the various feedstocks.

Some details of the gas composition are given in Table III. Hydrogen to carbon monoxide ratios are not materially affected by a change in coal feed compostion.

Removal of Sulfur and Nitrogen Compounds

After removing the solids from the raw gas, the gas still contains hydrogen sulfide, carbonylsulfide, hydrogen cyanide and ammonia which have to be removed. The processes used for their removal will depend on the particular application of the gas produced. The scheme discussed here is typical for a case where deep sulfur removal and minimum SO_2 emission are required (see Figure 3).

Sulfur Compounds

Sulfur is present in the gas leaving the gasifier as H_2S and COS, the H_2S/COS volume ratio being about 10-20. The absolute concentrations of both components depend primarily on the sulfur content of the coal and to a lesser extent on the composition of the ash. Both H_2S and COS can be effectively removed by a wash with modified Sulfinol. The bulk of the COS is hydrolyzed and in the end all sulfur containing components leave the gas treating section in the regenerator off-gas. Provided that the ratio between H_2S and CO_2 is above 1/6 the modified Sulfinol process features a simple line-up and enough selectivity to produce a regenerator off-gas with such a concentration of H_2S (minimum 45%v) that it can be directly routed to a Claus plant with a straight-through operating mode.

For coals which yield gases with a H_2S/CO_2 ratio of below 1/6 (low rank coals and/or low sulfur coals, e.g. the gas composition for German brown coal, see Table III), an enrichment stage has to be inserted between the H_2S removal and the Claus plant in order to produce a gas with a sufficiently high H_2S content for the Claus plant. Alternatively, oxygen enriched air may be used in Claus plant.

Nitrogen Compounds

Most coals contain at least one percent weight nitrogen and about 10% of this nitrogen is converted into HCN and NH_3 upon gasification. The rest of the nitrogen is converted into elemental nitrogen. Both HCN and ammonia are removed from the gas with water scrubbing.

The first stream in which part of the HCN, virtually all NH_3 and also part of the H_2S, CO_2 and all of the chloride is absorbed, is the water bleed of the solids removal system. This water which also contains solids is sent to a (normally two stage) sour water stripper. The gas free water slurry is then further routed to water treating.

The remaining traces of ammonia are removed from the raw coal gas in a second water wash the main purpose of which is to remove HCN from the main gas stream. The wash water is stripped in sour water stripper II and recycled to the HCN/NH_3 wash.

The off-gases from the sour water strippers and from the modified Sulfinol regenerator are sent to a Claus plant for sulfur recovery. The slurry sour water stripper for a high chlorine coal consists of two stages, a first stage in which the acid gas components are removed from the water, and a second (basic) stage in which the ammonia is recovered. The ammonia will often be partly recycled to the wet solids removal system for pH adjustment, the balance of the ammonia being incinerated with minimum NO_x formation. The combined off-gases from the acidic SWS and from the HCN wash stripper contain about 20%v HCN which may give serious problems in the Claus plant. Therefore these gases may be first sent to a catalytic conversion step where HCN is converted. The gases leaving the reactor are then combined with the H_2S rich gas from the Sulfinol regenerator and routed to the Claus plant. In the Claus plant about 90-95% of the sulfur is recovered as elemental sulfur. By including a Claus off-gas treating as e.g. SCOT[1] this percentage may be improved to 99.8%.

Waste Water Treatment

The potential sources of water in an SCGP unit are:

1. steam in the product gas leaving the reactor;
2. steam condensed in the slurry strippers;
3. storm run-off;
4. incidental waters.

Other water streams like the slagbath water, water from the wet solids removal system and water from the HCN-wash, are recycled within the gasification and treating stages.

Deep solids removal before biotreatment is achieved in a flocculation sedimentation unit. The sediments are filtered and sent to solids work-up. The last treatment steps before the water discharge into the environment are biotreatment under extended aeration followed by an after aeration (see Figure 4). With some coals there may be levels of inorganic pollutants remaining that require control technology beyond biotreatment.

Slag and Fly Slag Removal

By recycling solids removed from the gas in the cyclone back to the reactor and by injecting a concentrated slurry upstream of this cyclone it is in principle possible to convert virtually all ash in the coal into slag leaving the bottom of the reactor. This slag has very favorable leaching properties as is shown in Tables IV-VII.

Although the above system may work for certain ashes, there are indications that for ashes which are rich in iron, volatile metals or metal compounds such as zinc and lead (compounds) the above system may require a fly slag bleed to avoid build-up of these volatile compounds in the system.

Another complication may arise with ashes which are rich in limestone and/or dolomite. Inert slag is difficult to produce from these ashes.

1. Shell Claus Off-gas Treating process.

In the above reasoning it has been assumed that the slag will eventually be disposed of in an acceptable land fill area. It is obvious that for each specific case the possibility of using the solid waste material as a raw material will be investigated. Examples of such applications are e.g. cement and brick manufacture, and road building.

Options for Process Utilization

It is a matter of process optimization to assess for each project the most economic combination of heat recovery, power generation and treating temperatures in accordance with the economic yardsticks prevailing.

Some examples of Shell Coal Gasification Process utilization are briefly reviewed below.

Production of Fuel Gas, Gas for Direct Iron Ore Reduction, Syngas, Hydrogen and SNG Using a Gas Quencher

Oxygen-blown gasification using a gas quench and a waste heat boiler (see Figure 5 for flow scheme) coupled to processes for the removal of sulfur compounds, CO_2, HCN and NH_3 produces a dry gas typically consisting of 30-34%v H_2, 62-64%v CO and a few percent of inerts. The gas as such is very suitable as medium BTU fuel gas and reduction gas. The gas can also be enriched in H_2 by applying a CO-shift and a second CO_2-removal step. This gas can be used for the production of ammonia, methanol, liquid hydrocarbons and SNG.

The absence of methane in the raw gas, an ostensible drawback of the Shell Coal Gasification Process in the manufacture of SNG, is largely outweighed by the relative simplicity of the processing of the gas.

Production of Syngas, Hydrogen and SNG Using a Water Quench

As shown in Figure 6, another option for producing hydrogen or hydrogen rich gas is to use a water quench and to apply a CO-shift conversion with a sulfur tolerant catalyst followed by a selective H_2S and CO_2 removal.

Integration of Shell Coal Gasification Process with Combined-Cycle Power Generation

The integration of the Shell Coal Gasification Process and electricity generation in a gas-turbine/steam-turbine cycle offers an efficient and environmentally acceptable means of meeting future energy requirements.

The process lends itself to full utilization of the high efficiency of gas turbines with high inlet temperatures owing to the high proportion of electricity generated in the gas turbine, viz. up to 50% in an advanced scheme (see e.g. Figure 7). At the same time an efficient steam cycle can be maintained by the production of high-quality steam in the waste-heat boiler of the gasifier.

The particulate-free pressurized fuel gas produced in the gasifier is a low/medium BTU fuel gas which gives a low production of NO_x in the gas turbine combustor.

TABLE I

SHELL COAL GASIFICATION PROCESS
COAL FEED ANALYSIS

	Illinois No. 6 Bituminous	Wyodak Subbituminous	Coal Liquefaction Vacuum Bottoms	German Brown Coal	Auguste Victoria German Bituminous Coal
Carbon (%w MAF)	78.1	75.6	87.1	67.5	85.5
Hydrogen	5.5	6.0	5.7	5.0	5.2
Oxygen	10.9	16.8	3.3	26.5	6.5
Sulfur	4.3	0.9	2.4	0.5	1.1
Nitrogen	1.2	0.7	1.5	0.5	1.7
Ash (%w as received)	12.0	5.9	17.6	6.4	5.6
Moisture (%w as received)	6.5	35.0	0	60.0	6.5
Moisture (%w of coal to gasifier)	2.0	2.0	0	5.0	2.0
Lower heating value of coal as received in MJ/ton	25800	17160	29410	9990	29980
in BTU/lb	11095	7380	12645	4295	12890

TABLE II

SHELL COAL GASIFICATION PROCESS

COAL, OXYGEN AND STEAM REQUIREMENTS FOR DIFFERENT COALS

in metric tons per million Nm^3 $CO + H_2$ produced

Constant Plant Capacity	Illinois No. 6 Bituminous	Wyodak Subbituminous	Coal Liquefaction Vacuum Bottoms	German Brown Coal	Auguste Victoria German Bituminous Coal
Coal intake (to the complex) as received	573	810	494	1364	499
Coal to gasifier	477	489	494	626	447
Oxygen demand (99% vol pure)	400	395	407	434	430
Steam demand	36	12	86	20	44
Thermal efficiency, % (LHV basis) gasifier proper	83	83	83	79	83
Overall plant after subtraction of own consumption (e.g. coal drying, oxygen plant), % (LHV basis)	78	77	77	72	78

TABLE III

SHELL COAL GASIFICATION PROCESS

WET SYNTHESIS GAS COMPOSITION

Component %v	Illinois No. 6 Bituminous	Wyodak Subbituminous	Coal Liquefaction Vacuum Bottoms	German Brown Coal	Auguste Victoria German Bituminous Coal
H_2O	1.5	2.6	2.1	11.3	2.2
H_2	31.6	32.5	33.6	26.9	30.8
CO	64.0	62.8	61.8	55.0	64.7
CO_2	0.8	1.3	1.0	6.1	1.2
CH_4	--	--	0.1	--	--
H_2S + COS	1.4	0.3	0.7	0.2	0.3
N_2	0.5	0.3	0.5	0.3	0.6
A	0.2	0.2	0.2	0.2	0.2

Table IV

SLAG AND FLY SLAG COMPOSITION FROM AUGUSTE VICTORIA COAL

Sample		Slag	Fly Slag
	C %w	0.08	62.7
	H	0.01	0.3
	S	< 0.1	0.4
	N	< 0.3	0.5
	Cl	< 0.2	< 0.2
	O %w	50.9	18.8
Quantometer	Al %w	11.9	6.8
	Ba	0.14	0.09
	Ca	2.6	0.9
	Co	0.02	---
	Cr	0.2	0.01
	Cu	0.01	0.02
	Fe	8.0	2.6
	Mg	0.9	0.3
	Mn	0.08	0.02
	Mo	--	0.002
	Na	0.8	0.5
	Ni	0.02	0.02
	Pb	---	---
	Si	16.2	7.7
	Sn	---	---
	Sr	---	---
	Ti	0.4	0.3
	V	0.03	0.02
	Zn	---	---
	Zr	0.08	---
	Total	92.4	102.0
Atomic absorption	Cu mg/kg	147	148
	V	290	196
	As	15	11.5
	Cd	< 0.4	20
	Hg	0.15	0.07
	Pb	< 5	48

TABLE V

SLAG LEACHING WITH SYNTHETIC SEA WATER

TEMP. 100°C, LEACHING TIME 14 DAYS

	blank	Synthetic Sea Water exp. 1	exp. 2
pH start	8.2	8.2	8.2
pH end	---	6.1	6.3
TOC, mg/l	< 2	< 2	< 2
Cu, ppb	9	2	2
V, ppb	<10	<10	<10
As, ppb	8	1	8
Cd, ppb	<0.7	<0.7	2
Hg, ppb	<0.1	0.2	0.2
Pb, ppb	7	< 2	nd

nd = not determined

TABLE VI

SLAG LEACHING: DEMINERALIZED WATER

TEMP. 100°C, TIME 14 DAYS

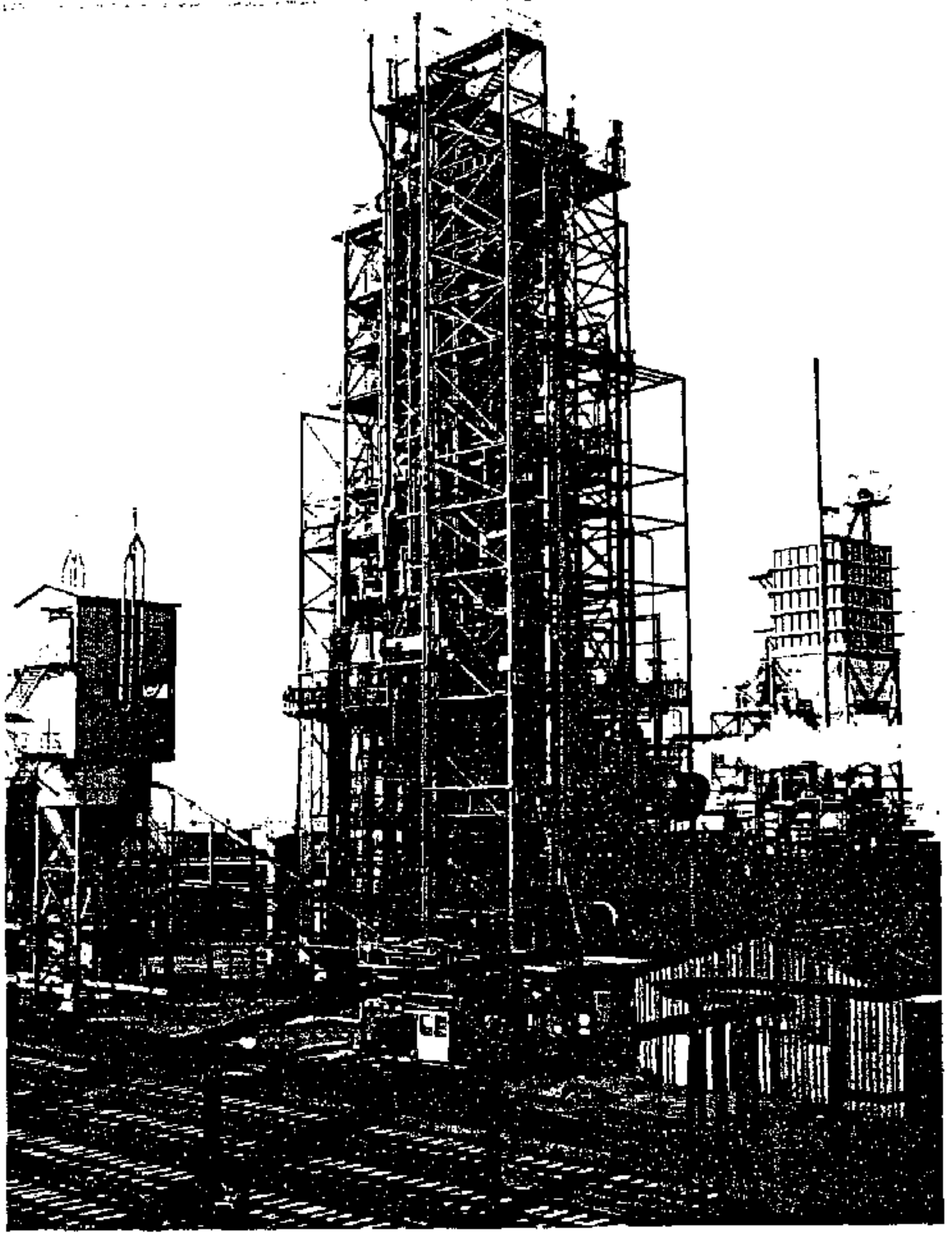
	Nitrogen	Air
	H_2O	H_2O
pH Start	6.7	6.5
pH End	8.5	8.7
TOC, mg/l	3	2
Cu, ppb	2	<1
V, ppb	<20	90
As, ppb	<1	2
Cd, ppb	<0.6	<0.6
Hg, ppb	<0.1	<0.1
Pb, ppb	3	<2

TABLE VII

LEACHING OF FLY SLAG

TEMP. 100°C, TIME 14 DAYS

	Demineralized Water		Synthetic Sea Water	
	Blank	Fly Slag	Blank	Fly Slag
pH Start	6.6	6.6	8.2	8.2
pH End	---	10.1	---	7.8
TOC, mg/l	3	2	< 1	5
CU, ppb	2	2	6	2
V, ppb	< 3	262	< 1	34
As, ppb	< 2	18	8	14
Cd, ppb	< 1	< 1	0.3	4
Hg, ppb	<0.2	<0.2	<0.2	<0.2
Pb, ppb	< 2	< 4	5	<3



Shell-Koppers coal gasification
150 T/D pilot plant at Deutsche Shell's Harburg Refinery

FIGURE 1

SHELL COAL GASIFICATION PROCESS
TYPICAL FLOW SCHEME

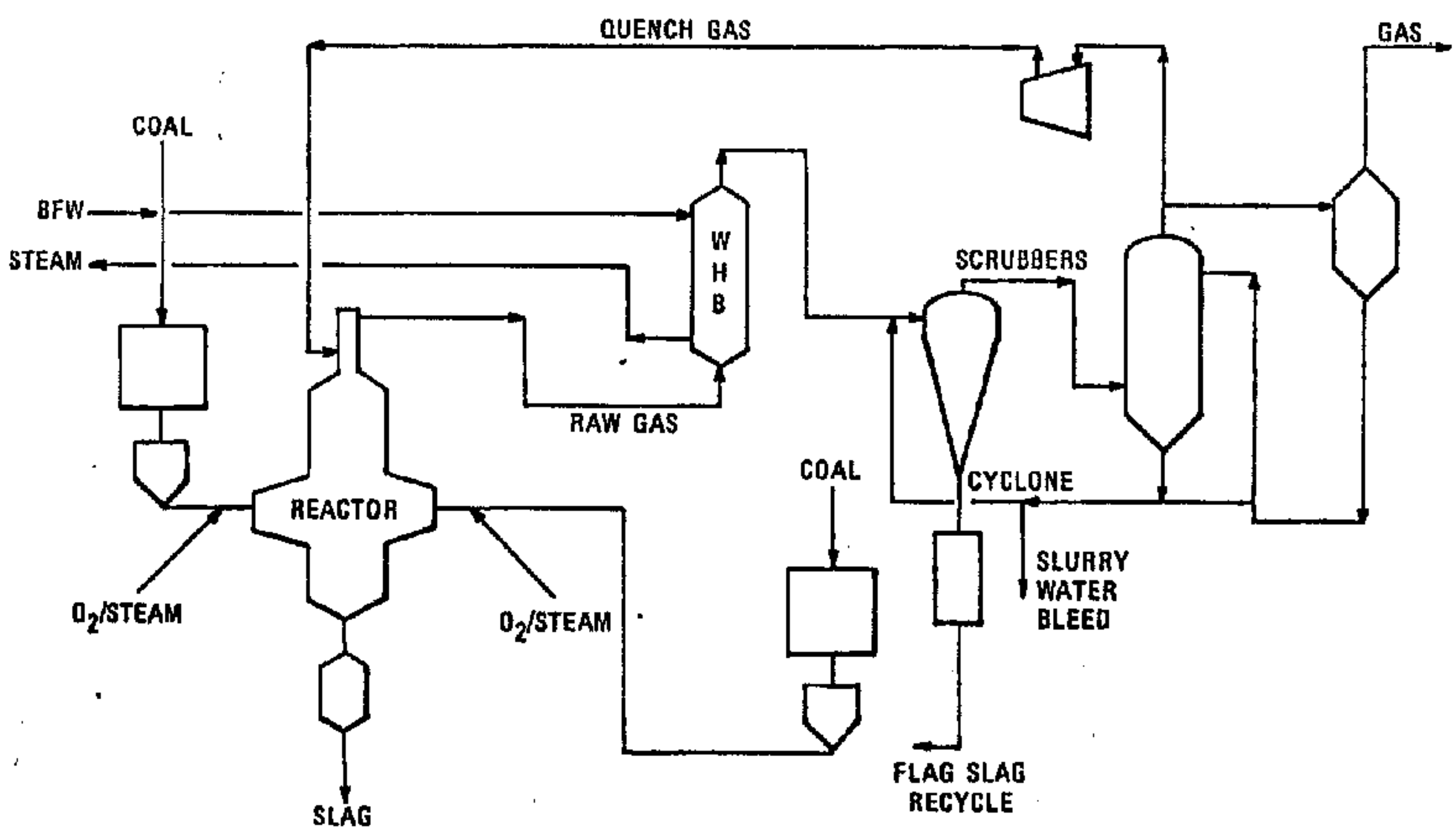


Figure 2. Shell Coal Gasification Process
Typical Flow Scheme

SCHEMATIC FLOW DIAGRAM OF THE INTEGRATED GAS TREATING AND WASTE WATER STRIPPING SECTIONS

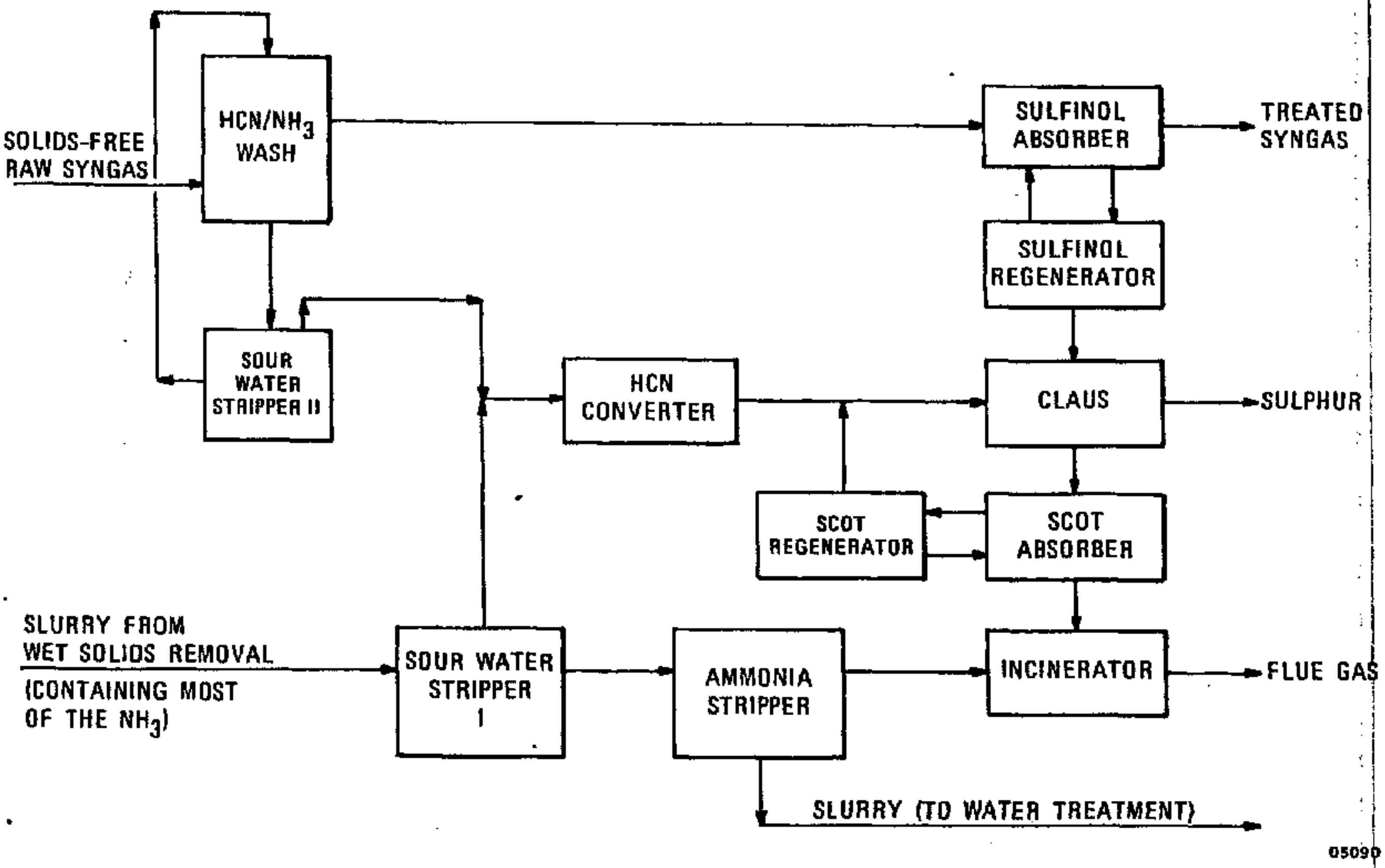


Figure 3. Schematic Flow Diagram of the Integrated Gas Treating and Waste Water Stripping Sections

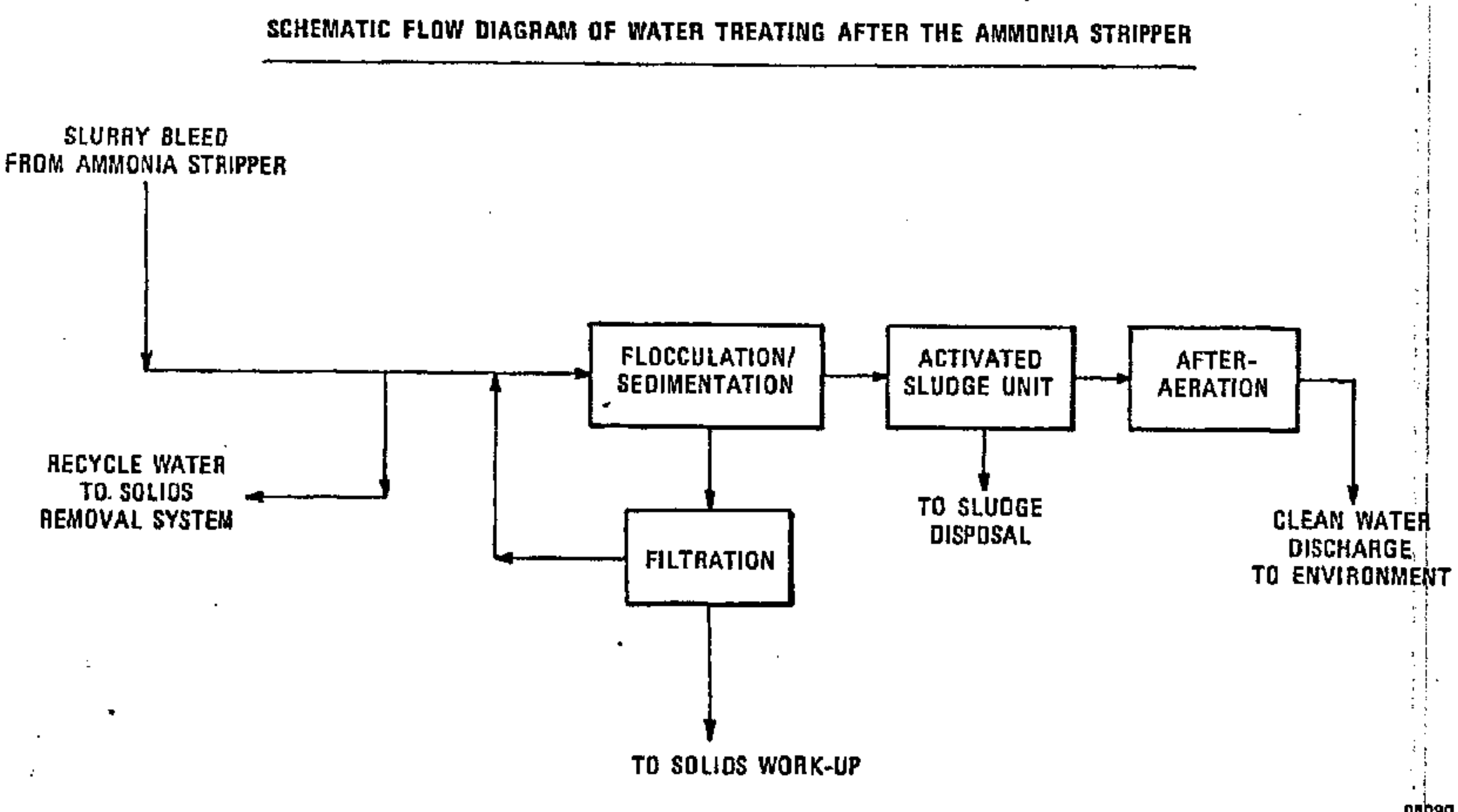


Figure 4. Schematic Flow Diagram of Water Treating After the Ammonia Stripper

BLOCK SCHEME FOR FUEL GAS OR SYNTHESIS GAS PRODUCTION, FEATURING A GAS QUENCH AND A WASTE HEAT BOILER

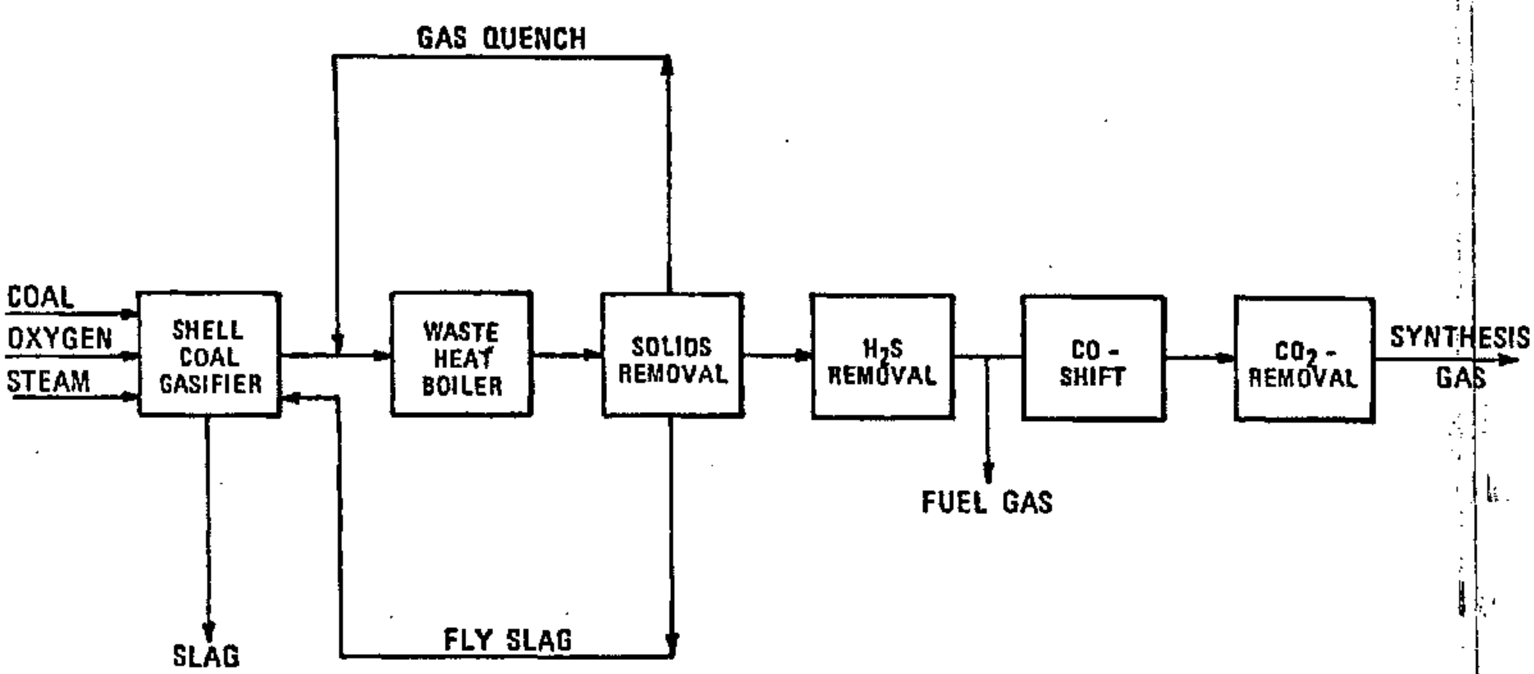


Figure 5. Block Scheme for Fuel Gas or Synthesis Gas Production, Featuring a Gas Quench and a Waste Heat Boiler

BLOCK SCHEME FOR HYDROGEN OR SYNTHESIS GAS PRODUCTION, FEATURING A WATER QUENCH

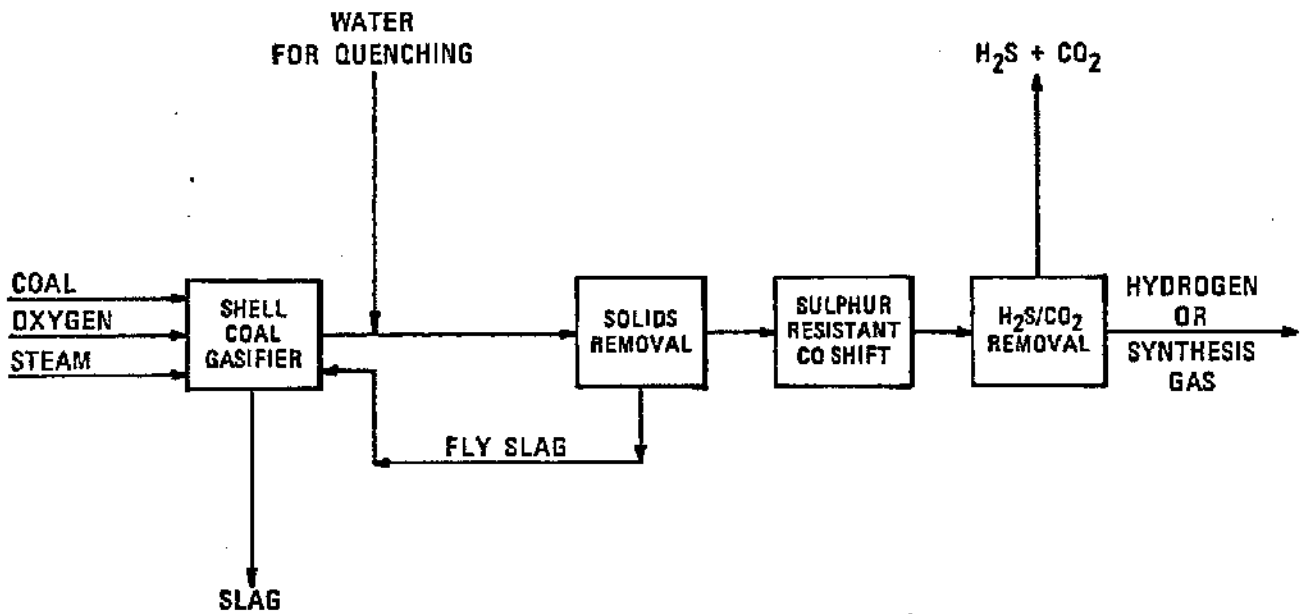


Figure 6. Block Scheme for Hydrogen or Synthesis Gas Production, Featuring a Water Quench

SHELL COAL GASIFICATION PLANT–COMBINED CYCLE POWER

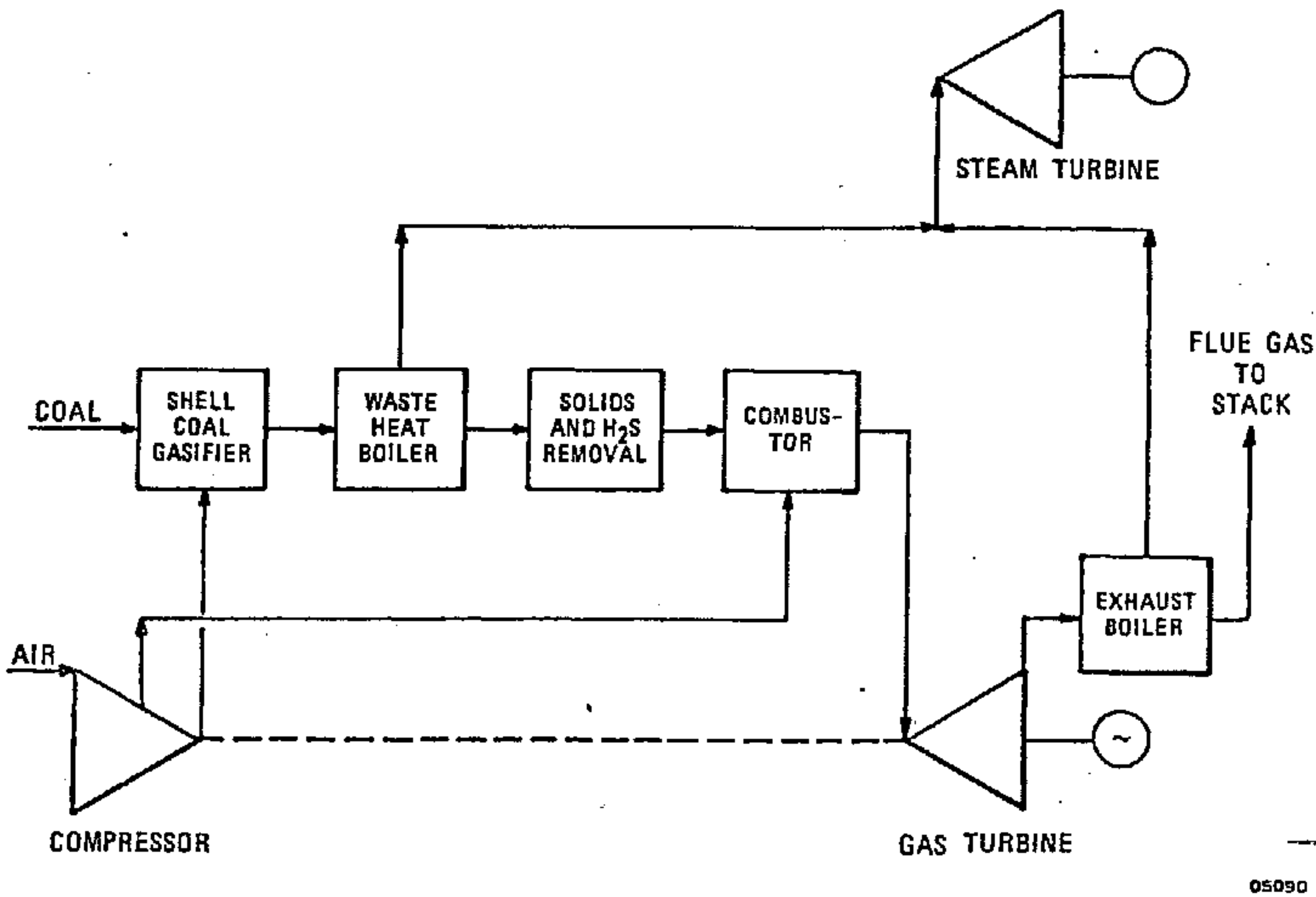


Figure 7. Shell Coal Gasification Plant-Combined Cycle Power