Present state of the synthesis of hydrocarbons by the Ruhrchemie synthesis (Fischer-Tropsch).

a.) Gas production.
b.) Removal of sulphur.
c.) Synthesis.
d.) Separation of products.
e.) Further treatment.
f.) Consumption of raw materials and energy.
g.) Capital cost and iron required for the erection of a synthesis plant.
h.) Manufacture of catalyst and regeneration of the spent mass of the benzine synthesis.
i.) Summary of principle apparatus.
k.) Manufacture of fine purifying mass for the removal of the residual sulphur from the synthesis gas of the benzine-plant.

Report according to article IV.
of the agreement
between
U.S.A.C. and R U H R C H E M I E.

a.) Gas production.

The raw material necessary for the process is a synthesis gas which contains CO and H_2 in the proportion of about 1 : 2. The process is not bound to an exact maintenance of this proportion. With a lower content of hydrogen in the synthesis gas, the hydrocarbons formed contain more olefines.

For the production of the synthesis gas, any fuels which may be gasified with steam can be used.

The following types of fuel may be applied:

1.) Coke. (High temperature coke or low temperature coke made from black-coal or brown-coal.)

In normal water-gas generators it is possible to produce from this fuel a watergas in the proportion of about 1 volume of CO to 1.25 volumes of H_2. The proportion necessary for the synthesis namely 1 volume of CO to 2 volumes of H_2 can be attained by the addition of a gas rich in hydrogen which is e.g. produced by converting a part of the watergas.

These raw materials can also be gasified under pressure with oxygen and steam so that immediately synthesis gas is obtained.

2.) Coke together with coke oven gas.

Without converting the raw material it is possible to produce immediately a synthesis gas if the proportion of coke to coke oven gas is adjusted accordingly. The coke is gasified in normal water-gas generators. The cracking of the coke oven gas may be carried out in the most different ways. The cracking can e.g. be effected in water-gas generators or in special cowper-stoves, where the cracking is carried out under high pressure. Coke oven gas can also be converted in a so-called "Zweischachtofen" (double shaft furnace) with oxygen and some coke immediately into synthesis gas.

3.) <u>Non-coking black-coal.</u>

By the gasification with steam, synthesis gas can also be produced from non-coking black-coal, the various gasification processes requiring different sizes of grains and ash melting points.

According to the properties of the coal, various gasification processes may come under consideration:

Chamber oven heated from outside,

flushing gas gasification,

gasification with oxygen and steam,

or also normal water-gas generators if the lump-size of the coal, strength of gasification and ash melting point are sufficient for this method.

4.) <u>Brown-coal: lignitic in the form of briquettes or dust.</u>

Also the peat may be included in this fuel group. The gasification of brown-coal can also be carried out according to the same processes mentioned under 3.), except in water-gas generators. Furthermore brown coal in dust form may be gasified. All processes of gasification stated above give immediately a synthesis gas.

5.) <u>Natural gas, cracking gas of oil cracking-plants, residual gas of the synthesis</u>

and similar gases may be used for the production of synthesis gas by making use of steam or carbonic acid and oxygen. The utilization of cracking gases and residual gases of synthesis plants for the production of synthesis-gas renders possible a saving in gasifying coal of 1o - 15 %.

b.) <u>Removal of sulphur.</u>

As any sulphur content at the synthesis has a dangerous effect upon the catalyst, the sulphur is removed in two stages, in a primary and a final purification plant

before the synthesis takes place so that the synthesis gas
contains less than 0,2 gram per 100 cu.m. The removal of
the hydrogen sulphide is carried out according to the pro-
cesses known in the gas industry e.g. by means of bog iron
ore or washing. The final purification for the removal of
organic sulphur is done according to our process by means of
a special absorption material. The process works as follows:

The synthesis gas freed from hydrogen sulphide is
heated in a tubular contrivance to an average of about 230° C
and flows through two fine purifiers which are connected in
series. The gas heater is fired with residual gas from the
synthesis. The purifying mass can take up 10 % of its own
weight of sulphur and must then be replaced by a new material.
The life of the purifying mass therefore depends upon the
amount of organic sulphur in the synthesis gas.

It is of utmost importance that the synthesis gas
does not contain any gums which would be dangerous for the
fine purifying mass as well as for the synthesis catalysts.
The gums may occur at the gasification of brown-coal and
black-coal and at the cracking of coke oven gas. If the for-
mation of gums cannot be hindered by a suitable operation of
the gasification process, the gums may be removed by making
use of activated carbon.

The efficiency of the final purifier is improved
by the addition of small quantities of oxygen or air to the
synthesis gas. The addition of oxygen amounts to about
0.2 to 0.4 % of the throughput of synthesis gas.

Apparatus of the fine purifier

Each set of the fine purifier comprises:
the gas heater fired by gas   according to drawing ZM 106/5,
2 fine purifiers according to drawings ZM 106/2 and 3,
1 heat exchanger according to drawing ZM 106/4.
The above constructions have a throughput capacity
of 20,000 to 25,000 normal cu.m. per hour of synthesis gas
in each set.

The gas heater is designed so as to heat the gas to
a maximum temperature of 350° C. The actual gas temperature

at the average   of the operating period is
about 275° C. The heating gas requirement amounts at an
average to about 1oo kg.cals. per normal cu.m. of synthesis
gas. Usually the residual gas of the synthesis is used for
heating purposes.

The gas heater essentially consits of the combustion
chamber lined with refractory brickwork, fitted with the gas
burner, the combustion air fan and the flue gas circulating
blower. This blower is designed in such a way that the tem-
perature of the combustion chamber can be kept at 8oo -
900° C. The gas supply is determined by the desired tempe-
rature of the synthesis gas. The gas heater itself is con-
structed as a tubular heater according to drawing ZM 1o6/5.
The tubes must be made of heat resisting material. Special
care must be paid to the expansion of the tubes.

Two kinds of construction may be used for the fine
purifiers.

The charging tower according to drawing ZM 1o6/3
holds the purifying mass which is contained in removable
screen trays which are taken out from the tower jacket by
means of a crane for filling and discharging purposes.
These trays are sealed against the clean gas chamber by means
of cups which are filled with fine granular purifying mass.
Each tower contains 65 - 7o tons of fine purifying mass.

The crude gas enters at the bottom of the tower and
distributes within the inner cylinder over the four screen
trays.

The crude gas distributes through four vertical
gas channels at the circumference of the inner cylinder. The
clean gas flows through the holes into the outer annular
space of the fine purifier, thence to the gas outlet.

The cover of the fine purifier is likewise fitted
with a ring cup which seals the crude gas section from the
clean gas compartment. The cover is provided with springs
to take up the heat dilatation of the system.

The second mode of construction according to
drawing ZM 1o6/2 now provides for two perforated sheet cylin-
ders which are shifted into each other instead of using the
screen trays containing the fine purifying mass. The fine

purifying mass lies in the annular space between the two per-
forated sheet cylinders. The inner perforated sheet cylinder
is divided into several sections which can be removed from
above. This construction makes it possible to discharge the
tower downwards through the inner perforated sheet cylinder.
The crude gas flows through the connecting piece "C" into
the outer annular space of the tower and from/there it is
uniformly distributed through the ringlike position of the
mass into the central tube in order to come out through the
connecting piece "F" as clean gas.

A disconnectable heat exchanger according to
drawing ZM 1o6/4 may be installed between the two purifiers.
It serves to preheat the incoming crude gas by means of the
hot gas from the firstly operated fine purifier tower. The
heat exchanger is built as a normal tubular heat exchanger.

The arrangement of a fine purifier group together
with the necessary pipe lines and fittings is shown on
drawing ZM 1o6/1. The gas flow is such that each of the two
purifiers can be operated as the first tower in the gas way.
The heat exchanger may not be used.

All parts through which flows the hot gas, are pro-
tected by a heat insulating material.

In order to obtain a more rapid cooling of a fine
purifier saturated with sulphur, a cooling system comprising
a recirculating blower and an ordinary washing cooler may
be built in. The cooling can be effected by the circulating
synthesis gas.

c.) Synthesis.

The synthesis gas is converted into condensable hydro-
carbons over a suitable catalyst in specially designed contact
chambers. The conversion takes place in two stages which
operate under similar conditions. The synthesis can be run
under atmospheric pressure at temperatures of 175 to 200° C
and gives a higher proportion of light boiling constituents
with a higher content of olefines. It may, however, also be
carried out at a somewhat increased pressure up to about
1o atmospheres, otherwise under equal conditions, which

results in a greater proportion of higher boiling hydrocarbons mainly of paraffinic character.

The yield of liquid primary products at the synthesis under atmospheric pressure is in operation about 120 grams per normal cu.m. of CO + H_2, in addition to about 10 grams of C_3 and C_4-hydrocarbons.

The life of the catalyst that means the operating period between two regenerations is about four months at the atmospheric pressure synthesis, whereas at the synthesis under increased pressure, the catalyst lasts about six months. At the synthesis under atmospheric pressure, it is advisable to treat after about 1,000 hours each for the hydrogenation of the paraffins condensed in the catalyst for about 10 to 12 hours with a gas rich in hydrogen which does not contain any carbon monoxide. The hydrogen used for such a hydrogenation amounts to 3,000 to 4,000 normal cu.m. for each treatment. The residual hydrogen from the catalyst factory may be used herefor. At this hydrogenation a part of the hydrogenation products is discharged in the form of oil from the furnace whereas the other part mainly consisting of methane is delivered to the residual gas.

At the synthesis under increased pressure such an intermediate hydrogenation seems hardly to be necessary according to our experience gained in practical operation.

The synthesis of hydrocarbons takes place under a considerable heat evolution. This reaction heat is utilized for recovering of steam under pressure. The steam pressure depends upon the reaction temperature in the synthesis and is normally 9 atmospheres. Approximately 5 kg of steam are generated per 1 kg of liquid primary products. This steam can be usefully employed at the various points of the plant.

The recovered liquid primary products include the whole group of hydrocarbons of C_5 up to the highly melting paraffins. The light boiling fractions contain at the synthesis under atmospheric pressure about 35 % of olefines whereas at the synthesis under increased pressure, the olefine index of this fraction only lies at about 20 %.

The attached tables 1 and 2 and the diagrams
ZM 106/16 and 17 show the average boiling analysis and other
characteristic features of the liquid products made for the
synthesis operating without pressure and for the synthesis
at increased pressure.

With a definite working method of the synthesis,
such as alteration of the specified load of the furnaces and
of the operating temperature and by altering the proportions
of CO : H_2, it is possible to effect certain changes in the
boiling range and in the olefine content of the product
against the normal values according to the tables 1 and 2.
These alterations result in increasing the oven temperature
and the specified oven load by which more light boiling
products are obtained whereas a reduction of the proportion
of CO : H_2 raises the formation of olefines.

Besides the liquid primary products and C_3 and C_4
hydrocarbons there is formed methane from a certain part
of the converted carbon monoxide with hydrogen. Furthermore
the oxygen-liberating at the cracking of the carbon monoxide
is fixed with a part of the hydrogen from the synthesis gas
into H_2O. The conversion of the charged carbon monoxide is
effected to the extent of about 9o %. The non-converted
portion of the synthesis gas together with the newly formed
methane goes to the residual-gas. According to the kind of
the synthesis gas charged, the quantity of residual gas
amounts to 3o to 15 % of the synthesis gas quantity having
a calorific value of about 2,ooo WE (heating units).

Apparatus of the synthesis process.

The contact chambers are supplied at the upper part
with synthesis gas which passes from the top downwards
through the catalyst. The catalyst rests upon screen trays
which can be opened so as to enable an easy downward dis-
charge. The reaction heat of the synthesis is transfered
to a water-cooled pipe system and led off in the form of
steam. The cooling system is therefore under pressure and
connected with a boiler drum according to the kind of steam
boilers which are fitted with the normal steam boiler ar-
matures.

The operating temperature of the catalyst can be easily controlled in the present case in that the steam pressure is regulated.

For the removal of the spent catalyst, the contact chambers are fitted with a trough from which the catalyst is delivered by means of a movable scrapper-conveyer to transporting vessels.

In case of the synthesis carried out under no pressure, the contact chambers are constructed according to drawings ZM 1o6/8, 13, 15.

The rectangular chambers are traversed by seamless boiler tubes in horizontal direction. Vertically to the tubes are steel sheets having a thickness of 1.6 mm being spaced at 7.4 mm. In order to obtain a good heat-transfer from the steel sheets onto the tubes, they are somewhat widened after fitting on the steel sheets, by putting a ball or the like through them.

The gas delivery pipe with installed orifice which allows to supervise the gas load in every chamber is situated in the removable cover. The cooling pipes project through the front walls of the contact chambers and are rolled into same. The cooling pipe ends of the collecting boxes are fitted into groups which are welded to the front wall of the synthe-sis chambers. These collecting boxes are connected with the boiler drum, similar to the sectional steam boilers.

The screen flaps which serve as a bearing face for the catalyst are built according to drawing ZM 1o6/1o so that they can be operated from outside during the run. Generally four synthesis chambers are combined to a block fitted with a common steam accumulator. Such an arrangement is shown on drawing ZM 1o6/7. The synthesis chambers are completely insulated.

At the synthesis under increased pressure, the contact chambers are carried out according to drawing ZM 1o6/14 and 18. They consist of wrought iron cylindrical boilers which are arranged vertically and which are fitted with a double pipe system between the two pipe plates as shown on drawing ZM 1o6/18. In the annular space between the inner and the outer tube there is the catalyst. The cooling water

takes up the space around the tubes and flows through the
inner tubes. In this way the reaction heat can be intensively
discharged. The system of cooling under the generation of
steam remains unchanged. Corresponding to the increased
pressure, also that section of the synthesis chamber being
under gas pressure must be resistant to compression. The gas
supply at these contact chambers is likewise done from the
top downwards. The arrangement of four such contact chambers
in one block is shown on drawing ZM 1o6/14.

As an example for the complete arrangement of a
large synthesis hall there is shown on drawing ZM 1o6/11 a
plant in half opened construction together with a non-pressure
synthesis section and a synthesis section working under in-
creased pressure. Open constructions are now under erection
and in operation at which only the service rooms are closed
whereas the synthesis chambers are placed outside.

Arrangement of pipe lines, auxiliary contrivances and super-
vision of operation.

At the two-stage synthesis, usually 8o - 7o % of the
synthesis chambers are operated in the first stage and 2o %
to 3o % in the second stage. It is advisable to carry out
the gas piping network in such a manner that 5o % of the syn-
thesis chambers can be used for the first and second stage
and only 5o % for the first stage.

The following contrivances are necessary for the
intermediate revivification of the catalyst in the synthesis
chambers.

A blower delivering hourly about 3,ooo normal cu.m.
of gas rich in hydrogen and free from CO boosts this gas
through a collecting pipe line to which every contact chamber
is connected through the hydrogenating furnaces. The paraffin
contained in the catalyst is thereby partly converted into
the lower boiling oil and partly to methane. Leaving the
synthesis chamber, the hydrogenation gas charged with oil
vapours is cooled in a scrubber and liberated from the with-
drawn oil. It then goes again to the circulation from which
each time a part of gas rich in methane is taken out and

replaced by fresh hydrogen. Each contact chamber has therefore
to be fitted with an inlet and outlet.

In order to be able to remove the paraffin collected
in the catalyst to a considerable extent by extraction before
the spent catalyst is removed from the furnace, a pipe line
shall be provided for which delivers the synthesis chambers
with heavy benzene.

It is preferable to connect each synthesis chamber
with a pipe line which carries protection gas such as carbonic
acid or nitrogen.

At the synthesis without pressure, all the hydrogens
manufactured are led off with the residual gas so that no
special pipe lines are herefor necessary.

At the synthesis under increased pressure about
35 % of the whole production of liquid hydrocarbons are al-
ready condensed in the contact chamber and are separately
discharged through a collecting pipe line from the bottom of
the contact chambers and delivered under pressure to the
vessels.

The remaining products are discharged with the resi-
dual gas of the synthesis and liquified in the condensation.

The following pipe lines are necessary for the
cooling system of the synthesis chambers:
Feed-water-lines, steam lines for middle pressure
and low pressure for the discharge of the steam generated in
the synthesis and a connection for high pressure steam to
each synthesis chamber for the heating-up, furthermore
sludge removing pipe line for the boiler and the condensate
discharge pipe line.

Automatic control.

For the operation of the synthesis, the temperature
in the contact chambers and the gas quantity put through each
furnace is of great importance. The temperature of the chamber
is controlled by an electrical or pneumatic valve which is
installed in the steam discharge pipe line of each oven block.
The regulation of this controlling valve is effected through

the pressure in the steam space of the boiler drum. The go-
vernor is to be so equipped that an easy adjustment of
pressure from 4 to 25 atmospheres is rendered possible.
The gas quantity put through each contact chamber is
determined by indicating orifice meters. For supervising the
gas conversion in the contact chambers, it is advisable to
instal a number of automatic instruments for the determination
of the CO_2- content in the end-gas after the synthesis cham-
bers. These instruments show the degree of conversion in each
individual oven. The degree of conversion of the gas in the
whole plant is determined by gas quantity meters before and
after each synthesis stage. These contrivances are most im-
portant for the control of the synthesis. Furthermore it
would be recommendable to adopt measuring devices for feed
water, steam, hydrogen, registration of the gas pressures
and steam pressures, contrivances for the examination of the
pressure loss in the gas during the passage through each
contact chamber.

d.) Separation of products.

1.) Synthesis at atmospheric pressure.

The synthesis products in vapour form together with
the residual gas are discharged from the contact chambers and
delivered to the cooling washers which are lined with acid
proof brickwork and which are packed with acid resisting
stoneware rings. The cooling washers are sprayed with water
which is in circulation. Thereby the hot synthesis gas is
cooled down and the heavy boiling fractions of the synthesis
product are condensed. The separation of the oil from the
wash water takes place in separate pits which are lined
with acid resisting bricks or in ordinary separating tanks
according to the specific gravity. The wash water is then
recooled and used again. The separated fractions represent
about 5o % of the whole product with an initial boiling
temperature of about 130° C.

The gases leave the cooling washers at a temperature of about 25° C and for the recovery of the light boiling fractions, they are washed-either with oil or in the well-known manner they are delivered to an activated-carbon plant. In both cases, the C_3 and C_4-hydrocarbons formed in the synthesis may be recovered to a great extent. The absorption of the liquid hydrocarbons is complete so that practically no loss of benzene does take place in the residual gas.

The liquid products recovered in the activated-carbon plant or in the oil washing plant represent approximately 5o % of the whole liquid products. In addition to same also propane and butane, propylene and butylene are recovered.

A special construction according to drawing ZM1o6/6 has been developed for the cooling washer.

Four supporting plates consisting of perforated sheet iron and an intermediate bubble tray are installed in the wrought iron jacket. The jacket including all connecting pieces and the bottom is lined carefully with acid resisting bricks, special attention having to be paid to the carrying out of this brick lining at the connecting pieces. The The carrying pawls and the carrying cross for the screen trays and for the bubble tray consist of sicromal steel. The tower is sprayed in three stages by means of the central water distributing nozzles. This device is likewise constructed of sicromal steel. The top spraying is supplied with fresh water while the two lower sprayings are fed with circulating water.

For the separation of washing water from oil tanks may be used which are lined with aluminum or pits lined with acid resisting brickwork. The separation of water and oil takes place very quickly so that the separating spaces are kept small. Sirce the greatest part of the organic acids developed in the synthesis remains in the circulating cooling water, it is advisable to manufacture the circulating water pumps and pipe lines of acid resisting material. The cooling device for recooling the circulating water must be built up of nails and anchors consisting of stainless steel.

The gas thus treated leaves the cooling washer at a temperature of about 25 - 30° C and withdraws all the hydrocarbons up to the final boiling point of about 170° C. The removal of these products from the gas does not necessitate any special contrivances. It is therefore unnecessary to give a detailed description just now.

2.) Synthesis at increased pressure.

Since the products at this operating method contain a high proportion of high boiling paraffins, about 35 % of the whole production of liquid products condense under the influence of the increased pressure in the contact chamber itself and are withdrawn from here in liquid condition. The initial boiling temperature of this part of the production lies at 200° C.

The remaining part of the hydrocarbons produced is extracted from the contact chambers together with the residual gas in vapour form similar to the synthesis which takes place under atmospheric pressure. If compared with the normal pressure synthesis, the condensation is facilitated by the increased pressure and can be carried along down to an initial boiling range of 140° C in the indirect coolers. Since the products as well as the reaction vapour carried along are acid, these coolers have to be constructed of acid resisting steel or a neutralisation must be carried out with alkalies in the first cooling stage. The proportion of liquid products thus to be condensed is about 45 % of the total production of liquid products.

The light boiling products including the C_3 and C_4 hydrocarbons can easily be extracted in an oil washing apparatus connected behind. The condensation combined with the oil washing can be arranged in such a way that automatically a certain fractionation of the products is obtained. Approximately 20 % of liquid products and 8 to 10 grams per normal cu.m. $(CO + H_2)$ C_3 and C_4-hydrocarbons may be produced in the oil washing.

e.) Further treatment.

The further treatment of the primary products depends upon the desired final products. As regards the possibilities of using the primary products they must be characterised as follows:

1.) Synthesis under atmospheric pressure. (see table 1.)

The recovered C_3 and C_4 hydrocarbons containing about 6o % of C_4 and 4o % of C_3 hydrocarbons of which 5o % each are saturated and unsaturated. The unsaturated hydrocarbons can be polymerized in the well known manner to the high valuable polymerization benzene. The saturated hydrocarbons are usually filled in liquid form into bottles under a pressure of 1o - 15 atmospheres and serve as liquid motor fuels for lorries or domestic gas for lightening and burning purposes.

The light boiling benzenes having a final boiling temperature of about 145° C and an octane number of about 6o according to the Research method recovered in the activated carbon plant or oil washing have only to be stabilized in order to give a finished motor benzene in the mixture with cracked benzene and polymerisation benzene or with benzol.

The liquid products which boil at a higher temperature than about 145° C consist of so-called paraffingatsch in the amount of 2o % with an initial boiling point of about 320° C and 4o % consist of a diesel-oil fraction boiling between 200° and 300° C, about 25 - 30 % of heavy benzene within the boiling limits of 14o - 200° C and about 5 - 1o % of intermediate fractions between 300° and 320° C.

As the octane number of the heavy benzene is very low it must be transfered by a reforming process in the oil cracking plant into an anti-knock benzene.

The diesel oil fraction has a cetene number of about 9o - 1oo and is in this way considerably higher than normal gas oils as regards the initiality. This fraction is therefore well suitable to improve inferior diesel oils or to produce a saleable diesel oil in a mixture with coal tar oil.

The paraffingatsch serves as raw material for the manufacture of plate paraffin with a melting point of 52° C and of hard paraffin with a melting point of $85 - 90^o$ C.

2.) Synthesis at increased pressure.

The products are mostly of paraffinic character according to the table 2. by increasing the proportion of heavy boiling products. In particular the proportion of the light benzene is considerably less than at the synthesis under atmospheric pressure whereas the proportion of heavy boiling paraffins is greater. Principally the possibility of utilizing the primary products is the same.

In accordance with the increased production of heavy boiling products it may be of economical interest to transfer the proportions boiling above 300 ^{o} C by a more gentle and thermical cracking essentially into diesel oil.

Cracking-benzenes from the primary products are refined sufficiently with bleaching clay and thereafter they are subject to a normal wash. The cracking benzene has a good reaction on the ordinary inhibitants. The sensibility of lead of the recovered benzenes is good.

f.) Consumption of raw materials and energy.

The requirement of synthesis-gas is determined by the formerly stated figures of yield. 10 - 15 % may be covered by the free residual gases of the benzene factory by means of cracking. 85 - 90 % have to be put available by the new delivery of fuels. The residual gas of the synthesis is partly used for heating the fine purifier, the oil distillation and the further treatment plants. The part produced beyond this amount can be used for the production of steam and electric energy as far as there is no utilization in the benzene factory itself.

The consumption of current at the low pressure synthesis is according to the kind of gasification process about 600 - 800 kWh per ton of motor benzole. This consumption can be fully covered from the steam obtained in the benzene factory.

At the synthesis under increased pressure the requirement of electric current is about 1,700 - 2,000 kWh per ton of motor benzole which depends upon the gasification process adopted. This energy required can fully be produced from the quantities of steam and residual gas obtained in the benzene factory itself, if no synthesis gas is manufactured from cracking and residual gases. In this case a part of the total quantity of energy must be seperately produced.

g.) Capital cost and iron required for the erection of a
    synthesis plant.

The invested capital of plants constructed range within about 600 Reichsmarks per ton of motor benzole using coke and coke oven gas as raw material. If brown coal is used as a raw material, the capital expenditures are higher up to 20 % on account of the higher cost for the gasification plants. The figures stated for the capital cost include the complete benzene synthesis, including gas production and treatment of products with all auxiliary plants except the plants for the manufacture of catalyst and of fine purifying mass. The figures have been based upon a plant capacity of about 50,000 tons of motor benzole per year.

The requirement of iron and steel for a synthesis-plant including the water-gas generators and the plants for treating the products amounts to about 600 kg per ton of year.

h.) Manufacture of catalyst and regeneration of spent
    mass of the benzine synthesis.

1.) General.

Apart from the conditions of operating the benzene synthesis and the composition of the purity of gas, the composition, structure and grading of the catalyst to be used for the manufacture of benzine are decisive factors for the yield and composition of the crude product obtained.

The contact mass essentially consists of amixture of cobalt, magnesium oxide and according to the local conditions

of larger and smaller additions of thorium oxide which in an extremely fine distribution is put upon a suitable carrier namely upon a kieselgur of certain structure and composition. The present contact mass consists of

> 200 parts of kieselgur
> 100 parts of cobalt metal
> 8 parts of magnesium oxide
> 2.5 - 5 parts of thorium oxide.

While the chemical composition is binding for the main constituents of the catalyst which analytically can be checked very easily, it is of course understood that besides the chemical composition also the number and kind of diatomaceous matter is of importance for the carrier that means only the catalytical examination itself decides upon its suitability in addition to a microscopic investigation. Actually the most different kinds of kieselgur have proved well useful for this purpose. Furthermore it often happens that useful kinds cannot be utilized directly for these purposes by a simple treating procedure.

The carefully manufactured catalyst which according to the working conditions can be kept in continuous operation for 5 - 7 months is subject after this working period to a regeneration process at which it is freed from foreign matter such as tarry constituents and sulphur and is placed upon new kieselgur.

The so-called catalyst factory must be used for the manufacture of new catalysts as well as for the regeneration of such catalysts which are discharged from the contact ovens after a certain running period.

After the first filling with new contact mass, the catalyst factory has mainly to regenerate the spent mass and only to manufacture that quantity of fresh cobalt which due to the unavoidable losses has to be replaced. These losses are due to the manipulations when filling and discharging the ovens as well as to such small quantities which are withdrawn in dust form with the synthesis gas and which are mainly found again

in the coolers and seperators. A small loss further results
from the regeneration of the contact mass. All these losses
are low as shown by experience and may be about 5 - 10 % per
year at a well operated plant.

2.) Manufacture of fresh catalyst.

This fabrication is used for the first filling of
contact mass into the newly started benzene plant as well as
to cover the above-mentioned losses which occur at normal
operation. The manufacture comprises the following:

a.) Solution of the elements provided for the manu-
facture of the catalysts, cobalt, magnesium oxide and some
thorium hydrocarbonate being principally dissolved in acid,
suitably in the most cases in nitric acid. After this, the
solution is cleared by means of filter-presses and if necessary
further freed from other chemical impurities e.g. lime if
latter should be present in the raw materials in larger
quantities.

b.) Standardization, dosage and precipitation of this
solution with soda and subsequent putting upon the carrier.
This manufacture is the most essential part of the catalyst
production. The working method is binding to obtain the pro-
per distribution over the carrier. Any faults made in this
connection have an effect upon the life of contact mass.

c.) After this procedure, the material is dried and
graded. Special care must be taken in order to obtain a uniform
and comparatively hard grain without destroying the surface
of the individual balls or gravels by the formation of a denser
layer. The dust formed is separated and returned.

d.) The so-called raw catalyst thus graded and dried
is subject in a reduction- plant to the effect of hydrogen at
certain temperatures and by taking great care of other con-
stituents, a certain part of the cobalt oxide and cobalt car-
bonate is transformed into metal.

e.) After a cooling of this hot catalyst with hydrogen
and nitrogen, the impregnation takes place with carbonic acid
or oil which permits to protect the contact mass from the
oxidation to such an extent that the transfer of the contact

into the transporting devices and later on the charging of this contact mass into the contact ovens may be effected without special protection means. During the transport and charging of the contact oven, a small addition of carbonic acid will be sufficient.

3.) Regeneration of spent contact mass.

The manufacture of the catalyst taking pure cobalt, magnesium and thorium as necessary for producing the first filling has been described in the foregoing. In order to be able to run the benzine synthesis for the normal operation it is necessary to revivify the contact mass coming from the contact ovens. Up till now it has proved as correct and economical to separate in the first line the cobalt quantity and a part of the magnesium as an acid solution and after a careful mechanical and chemical purification to put same into the process at point a.) of the above-described fresh manufacture.

A direct regeneration combined with the kieselgur has not given any good results, as with the acid concentration coming into question the activity of the contact mass thus regenerated suffers by the solution of certain constituents of the kieselgur. At the comparatively low cost of the necessary kieselgur it is advisable to separate same and to use it for other purposes (for insulation etc.). It has shown also as correct to separate a part of the magnesium during the cleaning process of the cobalt-solution and to extract it.

As the contact mass spent in the benzine plants naturally still contains a part of the products obtained during the manufacture primary stages must be provided for in the following sequence:

a.) It is recommended to oxidise carefully the contact mass discharged from the contact oven (should it happen that the catalyst is still pyrophoric) in a separate manufacturing stage of the so-called oxidation plant and eventually to remove the paraffin partly from the contact mass. Generally it is desired that the contact mass from the contact ovens is supplied with some paraffin and not ignitibly to the regeneration.

b.) The recooled catalyst is now treated in a so-called special solution station with acid whereby cobalt, magnesium and thorium dissolve, however, also a few constituents of the kieselgur. After this the kieselgur itself is separated in a filter-station.

c.) The solution obtained is freed from the greatest part of its impurities in a so-called first precipitating station, mainly from iron, aluminum and copper by a partial precipitaion with soda. Thereby all the thorium is likewise precipitated. The quantity of thorium contained in iron sludge is now treated in a separate station or if only a small amount of thorium is present, this sludge can be wasted or used for other purposes.

d.) The further purification is now effected by the addition of sodium fluoride in order to separate in the first instance certain quantities of lime which would have a detrimental effect upon the manufacture of catalyst in the further process.

The solution thus obtained is then identical to that produced from fresh cobalt so that the further process now proceeds as stated under 2.).

The accompanying flow sheet is a general view of the process of the contact mass manufacture.

i.) Summary of the principal apparatus.

The type and necessary number of the prinipal apparatus may be seen from the enclosed project drawings and sketches as well as from the production schemes and several workshop drawings.

The suitability of the use of various filter contrivances, certain presses etc. is dependent on the manufacturing capacity which is taken as a basis for the catalyst factory. Therefore a scheme has been prepared which can be used for a comparatively small plant and also an arrangement which provide for continuous processes if it is possible to erect a large scale manufacturing plant that means an installation of larger

settling tanks, Dorr-thickener etc. By this a considerable saving of labourers could be effected.

   The various stations are indicated on the drawings and the working process is clearly shown in the flow sheet.

   Rough sketches of arrangements are enclosed illustrating a comparatively small plant.

   Furthermore are fully shown:
Solution-vessels, precipitation tanks, filter-contrivances, reduction-plant and other auxiliary apparatus, the working method of which may be seen from the manufacturing scheme. A quantity flow sheet roughly indicates the proportions.

k.) Manufacture of fine purifying mass for the removal of the residual sulphur from the synthesis gas of the benzine plant.

   As may be seen from the foregoing, it is of utmost importance for the operating method of the catalyst in the ovens of the benzine plant that the synthesis gas to be converted is not only highly freed from the inorganic sulphur but also from all organic sulphur compounds if possible. This final removal takes place by the normal sulphur purification in a so-called fine purification plant at increased temperature in which a special mass is charged as catalyst which we call "fine purifying mass". The quantity of the required fine purifying mass naturally depends upon the composition of the gas or upon the coal, coke or other raw materials to be treated. At medium conditions with a gas quantity of 1oo,ooo cu.m. per hour to be treated one must reckon with a manufacture of about 1o tons of fine purifying mass per day. The finished fine purifying mass is of following composition:

   62 - 64 parts of lux mass
    33 parts Na_2CO_3
   3 - 5 parts of water.

   The manufacture is comparitively simple. The lux mass with a moisture content of about 5o - 6o % is mixed with a corresponding quantity of calcined soda that means according to the water content 1/4 to 1/5 of the weight of the

lux mass by the addition of the dust quantity returning from the grading plant, and kneaded in an Esch-mixer of well-known construction.

The raw mass thus made homogenous is distributed over a screen of special design and delivered to the drier. Here the mass is dried down to $3 - 5 \%$ H_2O.

The dried mass is brought to the desired grain size in a subsequent grading apparatus. This grain size must be larger or smaller according to the gas employed and the fine purifyers adopted.

For the time being we are obtaining good results in testing the manufacture of a granulated material instead of the grained and squared material. The arrangement of the apparatus as well as the construction of the most essential parts of the plant may be seen from the enclosed drawings.