7th April, 1938

LD-378

Dr. F. Ringer,
I.G. Farbenindustrie Aktiengesellschaft,
Ludwigshafen a. Rhein,

Catalytic Cracking

Dear Dr. Ringer,

We are attaching two copies of a memorandum by Mr. Murphree, dated March 28, discussing the possibility of using powdered clay as a cracking catalyst and the reasons why this is believed to offer possibilities of improved operation. We believe you will find this of considerable interest, especially as it is a method that is not covered by the Houdry patents and, if the conclusions drawn in the memorandum are sound, would be an advance in operating efficiency over the present methods by effecting a considerable reduction in coke formation.

We will be very interested to have your early comments on the memorandum.

Yours very truly,
W. C. ASBURY

y: D. A. L. Dewdney

DACD/JES
Enclosures (2)

MEMORANDUM

CATALYTIC CRACKING USING POWDERED CATALYST

A certain amount of data which has been accumulated in the cracking of gas oil vapor with pilled or extruded catalyst indicates that the use of powdered catalyst may have considerable application. This possible application rests on two factors:

(1) The possibility of using quite short times of contact;
(2) Reduction in coke formation per unit of gasoline produced due to both the gas oil vapor and the catalyst being in the reaction zone for a short time.

There is a certain amount of data which indicate that with pilled catalyst the amount of conversion of gas oil to gasoline is independent within limits of the time of contact of gas oil vapor and catalyst, and that it depends primarily on the amount of gas oil vapor subjected to cracking per unit of catalyst present per cycle. The following are representative data taken from the correlation curves of the Baton Rouge D & R Laboratory for cracking light East Texas gas oil with pilled Super-Filtrol clay:

Throughput: (Vol. of gas oil per vol. of catalyst per hour)	Gas Oil per Unit of Catalyst per Cycle					
	0.6 V/V		0.3 V/V		0.15 V/V	
	Time	Conversion	Time	Conversion	Time	Conversion
0.3	2	40%	1	44	0.5	50
0.6	1	32	0.5	38	0.25	50
1.2	0.5	27	0.25	35	0.125	50 *

* Extrapolated.

The above table shows data for three different quantities of gas oil subjected to cracking per unit of catalyst per cycle. For each of these different quantities of gas oil, data for three different throughput rates of feeding gas oil are given, expressed as volumes of gas oil per volume of catalyst per hour. Under each of the columns for a given quantity of gas oil per unit of catalyst per cycle, the time interval of the cracking cycle and the conversion obtained for each of the three different throughputs are shown. The product of the throughput expressed in volumes of oil per volume

of catalyst per hour and the time interval of the cracking cycle in hours gives the total volumes of gas oil per volume of catalyst per cycle corresponding to the particular column.

It will be noted that for 0.6 volumes of gas oil per volume of catalyst per cycle the conversion obtained decreases somewhat with increased rate of throughput. This tendency is less marked at 0.3 volumes of gas oil per volume of catalyst per cycle, and apparently disappears for a gas oil to catalyst ratio of 0.15 volumes of gas oil per volume of catalyst per cycle. Some of the data in this last column are extrapolated, and hence the conclusions are open to question. There is, however, a very definite trend that for increased quantities of olay per unit of gas oil cracked per cycle, the conversions for the given throughput rates come closer together. The data at the Esso Laboratories indicate this even more definitely than the data from the Baton Rouge Laboratories. since essentially the same conversion is obtained where the amount of gas oil cracked per cycle per unit of olay is low for widely different feed rates, this is a very definite indication that over the range covered by the data the degree of cracking is independent of the time of contact of gas oil vapor and olay.

In trying to picture the application of results obtained in cracking of olay pills to cracking with powdered catalyst, the following considerations may be helpful. In the first place all the cracking undoubtedly occurs at the catalyst surface and so long as this surface is exposed to gas oil vapor for a given time it should make no major difference whether gas oil is continuously passed over the surface or whether the catalyst mass is distributed uniformly through a volume of gas oil vapor corresponding to the amount passed over the catalyst in a given cycle. This might be more easily pictured by reference to Figure I which indicates a layer of catalyst pills and the volume of gas oil vapor which is passed over the catalyst in a given cycle. The assumption is that the cracking results would be the same if the individual pills were uniformly distributed throughout the volume of gas oil vapor shown in Figure I, and that the gas oil vapor and catalyst be kept in contact for the entire cycle time. If this assumption be accepted, then the data on cracking with pilled catalyst can be readily extrapolated to the use of powdered catalyst which would be suspended in the gas oil vapor. In this case the volume of gas oil per volume of catalyst per cycle is simply the reciprocal of the concentration of the olay in the gas oil vapor. The conclusions reached above in regard to the effect of time of contact on cracking with pilled catalyst would mean that for relatively high concentrations of olay or catalyst per unit of gas oil vapor, the conversion obtained would be independent of the time the catalyst and gas oil vapor were allowed to remain in contact. This leads to the interesting conclusion that provided the gas oil vapor and powdered catalyst are well mixed, the actual time of this mixture in a reaction chamber may be extremely small which means that the size of the catalytic cracking reactors could be reduced quite appreciably

Correlation of the best available information on coke forma-
tion during catalytic cracking indicates that the amount of coke
formed on the catalyst is a function of the time of contact of the
catalyst with gas oil vapor, and does not depend on the conversion
of gasoline obtained. Most of the catalytic cracking work has been
done at a temperature of 850°F. and there are not sufficient data
for other temperatures to indicate whether or not the amount of coke
formed per unit of time varies appreciably with temperature. The
fact that the amount of coke formed on the catalyst depends on time
of contact only and not on the degree of cracking means that the
mechanism of the cracking reaction and the mechanism of coke forma-
tion are separate. By having the catalyst in contact with gas oil
vapor for only a short time, the amount of coke formed per unit of
catalyst can be made quite small. It has previously been indicated
that the amount of gas oil converted to gasoline, using powdered
catalyst, does not depend on the time of contact provided reason-
ably high concentrations of powdered catalyst per unit of gas oil
are used. Taking these two factors into consideration, one is led
to the conclusion that the amount of coke formed per unit of gaso-
line can be greatly reduced by having the time of contact of both
the gas oil vapor and the catalyst in the reaction zone quite short.
If this is so, such a type of operation would lead to an appreciable
reduction in the cost of equipment for catalyst regeneration.

A curve showing the amount of coke formed on pilled upper
Filtrol clay during the cracking cycle is shown as a function of
time duration of the cycle in Figure II. For a half hour cracking
cycle at 850°F., the amount of coke formed on the catalyst is 1.1%
By reducing this time of exposure to clay down to say 5 seconds
an extrapolation of the curve would indicate that the coke forma-
tion would be 0.08 which is only one-fourteenth as much.

The time of contact of gas oil vapor with catalyst in the
experimental equipment in which gas oil vapor is passed through a
bed of pilled catalyst is of the order of magnitude of 15 to 30
seconds. It would therefore seem quite reasonable to reduce the
time of contact of gas oil vapor and clay where powdered catalysts
are used down to 15 seconds or less, possibly 5 seconds. The coke
reduction indicated in the preceding paragraph may therefore be
feasible. The use of powdered clay, as compared with pilled clay
may have particular advantage where the times of contact are short
due to the reduction in time required for gas oil vapor to diffuse
in and out of the catalyst.

There are any number of ways of contacting gas oil vapor and
powdered catalyst, and several are now being considered. One of
the most promising of these is the Fuller Kenyon type of pneumatic
conveyor system, where granular material (in our case clay) is
fed through a special fitting into a pipe by means of a compression
screw. Vapor (or in our case gas oil vapor) is introduced into

this same fitting. Over a relatively wide range of gas to clay the mixture will flow through the pipe. For catalytic cracking, we will have about 48 cu.ft. of gas oil vapor per cubic foot of catalyst. The Fuller Kenyon system has operated for transporting granular materials with 10 cu.ft. of air per cubic foot of granular material. This system therefore seems adaptable to the vapor-solid ratios which would exist in catalytic cracking. This type of equipment has been satisfactorily used for conveying powdered lime through a coil in which the lime is preheated to a temperature of 1400°F. For a large scale catalytic cracking plant, say one handling 20,000 B/D of gas oil, about seven 10 inch Fuller Kenyon systems would be needed to convey the amount of clay and gas oil vapor involved. The length of pipe the gas oil vapor and clay would have to flow through in each of these systems would depend on the time of contact required. While the indications from the existing data are that the time of contact can be made very short, this will have to be demonstrated experimentally.

A second form of apparatus for contacting gas oil vapor and catalyst is shown in Figure III. Here powdered catalyst is dropped down a tower through the gas oil vapor which is also flowing downward. The tower contains mixing paddles or fans for insuring intimate contact of vapor and catalyst. Still another form of equipment is the Jacob's ladder type indicated in Figure V. Here catalyst falls down against an ascending stream of gas oil vapor. Another type is indicated in Figures VI and VII. Figure VI shows a type of equipment discussed by the Brassert Company which consists of a horizontal cylinder containing revolving paddles which will throw powdered catalyst up into the gas oil vapor stream. Figure VII shows a type of conveyor that has been used successfully for cooling granular materials. A 16 inch diameter or larger pipe is rotated at reasonably high speeds to convey granular material from one end to the other. This conveying action is accomplished by means of pick-ups or flights welded inside the shell of the pipe. The vapor is passed through the pipe and intimately contacted with the catalyst which will be thrown into the vapor space by means of the pick-ups.

The regeneration of powdered catalyst looks as though it can be very readily accomplished. One means of carrying out this type of regeneration would be to use the Fuller Kenyon system of the same kind as may be used for the cracking operation. In this case the conveying gas would be air which may be partially diluted with inert gas or steam if desired. As the oxygen content is used up, additional quantities of air could be added throughout the length of the pipe. The heat of regeneration could be removed by cooling the surface of the pipe to the desired degree. This system has the objection that quite long lengths of pipe may be required to

remove the heat and also that the addition of air at a multiplicity of points may lead to difficulties in control. Another method of carrying out this regeneration, which at present appears more desirable is indicated in Figure VIII. Here powdered spent catalyst is introduced into an ascending stream of air which may be partially diluted with gas or steam. Due to the fine division of the catalyst the regeneration will probably be accomplished very rapidly. After going up through the trumpet type of pipe indicated, the gas oil and clay come down through a tubular apparatus where the heat of regeneration is removed. The clay is then separated out from the air and other gases in a separator and a portion of the combustion gases recycled. That portion of the combustion gases which is vented from the system to make room for the required quantity of fresh air must be subjected to careful separation of catalyst so that the loss of catalyst will not be excessive.

One form of catalytic cracking equipment for carrying out all the necessary steps, based on the use of the Fuller Kenyon conveyor system for the cracking step, is shown in Figure IX. Here provision has been made for removing gas oil vapor from the catalyst after the catalyst step by steam and also for removing air from the catalyst after the regeneration step by the same means. The quantity of catalyst actually contained in this system can be quite small, but the rate of catalyst circulation will be quite large. The most serious drawback to the use of powdered catalyst is in the possibility of loss of the catalyst in the vent gases from the regeneration step. Here great care to recover catalyst will have to be exercised.

The general conclusion we have reached from the above considerations is that the use of powdered catalyst may offer a means of greatly reducing the investment and operating costs in catalytic cracking equipment. We expect to try out the use of powdered catalyst in the laboratory within the next two weeks, and are at present working up a design of equipment suitable for application to the Hundred Barrel Plant at Baton Rouge.

E. V. MURPHREE

EVM.CBC
Enclosures
Copy to Messrs F. A. Howard
R. P. Russell
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C. L. Brown
E. J. Gohr
H. J. Hall
W. J. Sweeney
E. B. Peck

Figure I

Pilled Catalyst

Gas oil vapor

(a)

Pilled Catalyst distributed uni-formly through gas oil vapor

(b)

Figure III

Clay Hopper

Fuller Kenyon conveyor system.

Gas oil vapor in

to Cracking Coil
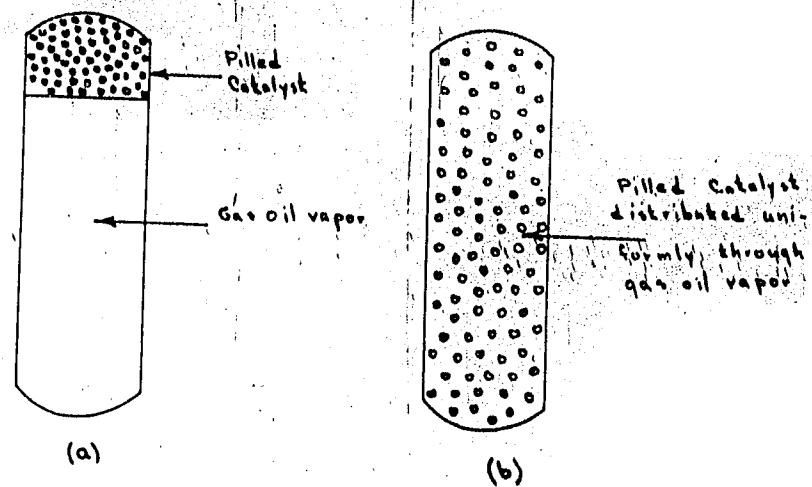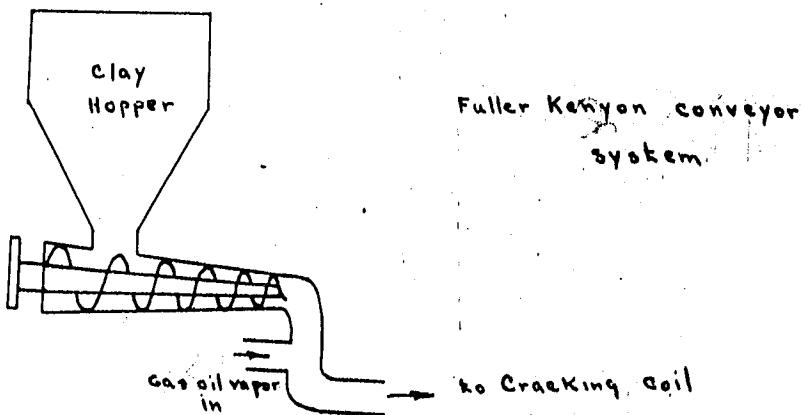
FIG-II

COKE FORMATION VS. TIME OF CRACKING

Figure IV — Agitated Contact Tower

Gas oil vapor in — Clay in — Gas oil vapor out

Figure V — Jacob's Ladder Type

Gas oil vapor out — Clay in — Gas oil vapor in — Clay out

Figure VI — Brassert Proposal

Gas oil vapor in — Clay in — Gas oil vapor out — Clay out

Figure VII
Conveyor Type

Clay in

Gas oil vapor in

Gas oil vapor and clay out
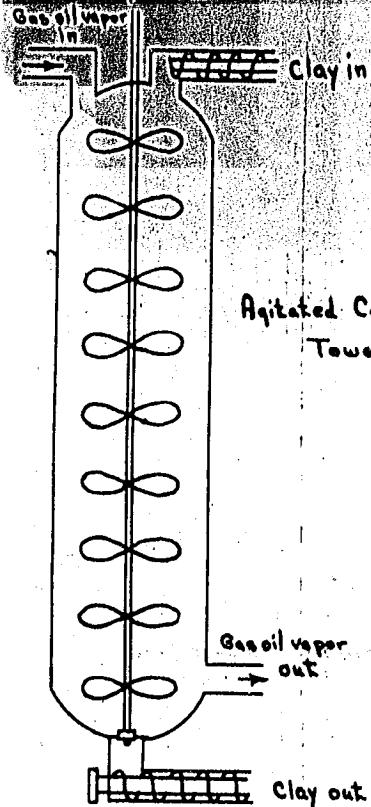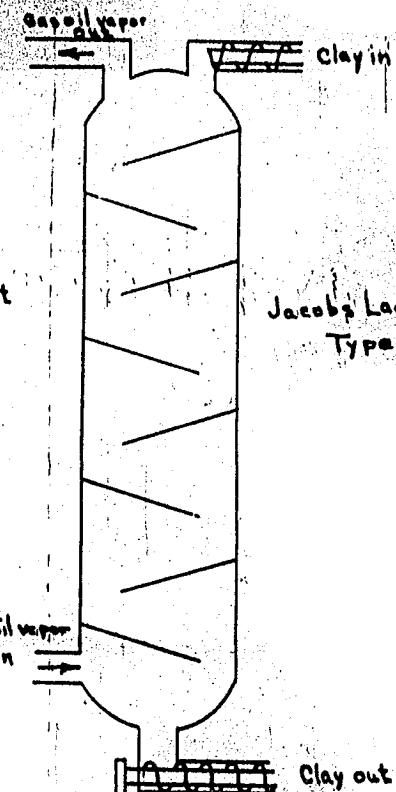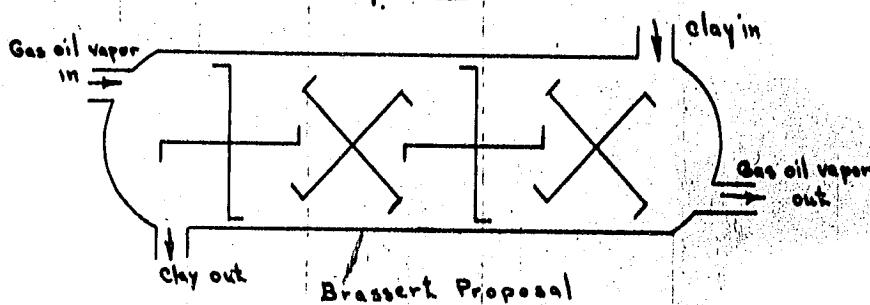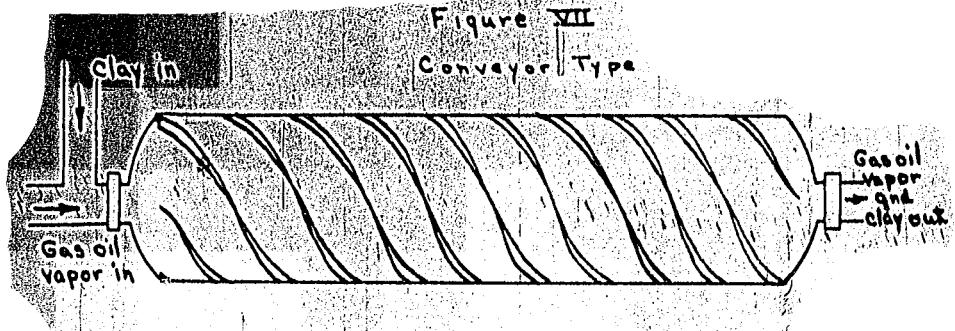

Figure VIII
Regeneration Apparatus

to atmosphere

Cottrell Precipitator

Heat Removal Tubes

Vent gas

Cyclone Separator

Recycle gas

Spent Clay in

Pump

Fresh air

Clay out

Clay out

Figure IX