1655

SINCLAIR REFINING COMPANY

S-10

Ruhrchemie A.G.
Oberhausen-Holten,
October 17, 1944

Experiment #808

100 Fe,5 Cu,10 CaO,30 Kgr (Precipitate of Sodium Bicarbonate) 1% KOH Impregnation.

Preparation of Catalyst #PN83 in Catalyst Laboratory of Rees. Confer Experiment #807

Pretreatment of the Catalyst with Water Gas:

1600 cm^3 (0.83 kg) of unreduced catalyst are filled into a 16-tube reactor. They are reacted with air (1500 l/hr) at 250° for 14 hours. Rinsing with nitrogen (100 l, 30 min.). Water gas is put through, maintaining the issuing quantity constant at 150 l/hr. Samples drawn after 2,4,6,8,10,13,15, 20,30,50,60 minutes. Up to the sixth minute practically all of the CO and H_2 was consumed. Much CO_2 and some methane were formed. Up to 30 minutes little methane was formed (0.5% in the end gas). The samples taken after 50 and 60 minutes showed 1.2% of methane in the final gas. Up to the sixth minute the end gas contained about 75% of CO_2; thereafter the CO_2 content decreased gradually to 13%. After one hour the water gas pretreatment was terminated. By putting through 50 l of nitrogen the temperature was reduced to 200°C within an hour.

Testing the Catalyst:

After reducing the temperature to 200°C and after rinsing with nitrogen, water gas was charged. A constant issuing quantity of 150 l/hr was maintained. After attaining 220°C (22 hours of operation) the conversion rate was 20% (methane volume = 11, working-up = 0.86). After increasing the through-put from 100 l/hr per 1 ltr. of catalyst to 200 l/hr, the conversion rate remained about the same. The methane formation decreased (mv = 8) and the working-up ratio improved to X = 0.93. After increasing the temperature to 230° the conversion rate averaged 30% (mv = 8; X = 0.86, A (yields) = 47/m^3). After 72 hours of operation we changed to synthesis stock. At 230°C and at a through-put of 200 l/hr per one l of catalyst the conversion rate was 32% (Mv = 7, X = 1.06; A = 47). The experiment was terminated because of the lack of water. resp. synthesis gas.

Assessment of the Catalyst:

The pretreatment with water gas at 250°C during one hour resulted in an active contact. At 230°, normal pressure, double charge with water gas: U (conversion rate) = 30, Mv = 8, X = 0.86, A = 47. With synthesis gas: U = 32, Mv = 7, X = 1,06, A = 47.

M. Beth

MB:op

SINCLAIR REFINING COMPANY

April 22, 1947 1657

S-11

Reel 42
Bag 3439-22
page 345

Ruhrchemie A.G.
Oberhausen Holten, October 19, 1944

Experiment #803
100 Fe, 5 Cu, 10 CaO, 30 Kgr (soda precipitation) potassium water glass impregnation (0.45 K/100 Fe.

Preparation of catalyst #PN78 in the catalyst laboratory of Rees.
Hot nitrate solution (1.8 kg Fe and the corresponding copper and calcium quantities) are poured into a boiling soda solution (6.4 kg of soda in 50 ltr of water). 540 g. of kieselgur are added. The mass is stirred for a short time and then filtered on a suction filter. It is washed with 10 x 10 l. of hot plain water (Water work of Rees, 30 mg of thloride per liter; total degree of hardness 22.96 German degrees; carbonate hardness 16.80; permanent hardness 6.16). Suspension in 100 l. of water-works water and once more filtering in the suction filter. The contact-cake formed is treated with 72 cm^3 of potassium water glass solution (342 g. SiO_2/l, 111 g k/l, 21 g Na/l/) which was diluted to 350 cm^3 previous to the impregnation, followed by handling in the kneading machine for 30 minutes. The cake is spread on sheets. Dried in the drier at 100°C, formed into 3 mm granules.

Pretreatment of the catalyst with water gas
Three reactors (each one containing sixteen tubes of 12 mm) are filled with 1600 cm^3, that is, 0.83 kg of catalyst each, that is a sum total of 4.8 l. of catalyst each (2.49 kg). We pass carbon dioxide until they are heated up to 250°C, then we shift to water gas. We adjust it for a constant end gas quantity of 150 ltr/hr. per reactor. Analyses of the issuing gases after 48 hours:

	a	b	c
CO_2	19.6	21.7	21.5
Cu H_m	1.1	1.1	1.2
O_2	0.1	0.4	0.2
CO	23.7	22.3	22.1
H_2	45.1	45.9	44.3
CH_4	2.9	2.9	3.4
C-Z	1.48	1.35	1.62
N_2	7.5	5.7	7.3

Termination of the pretreatment after 48 hours. Cooling in a slow water-gas current.

Testing of the catalyst

Three-step experiment, medium pressure, synthesis gas.

The catalyst which had been pretreated in three 16-tube 5 reactors was tested in the same reactors. Charging with a synthesis gas of 10 atü and heating up. After attaining a temperature of 150°, synthesis gas (500 l/hr.) is put through. The reactors are switched one behind the other; after the third step activated coal is applied. Slow temperature increase up to 200° within 12 hours of operation. First sample drawn behind the third step after 57 hours of operation (throughput; 570 N l/hr; conversion rate U = 31%; methane volume Mv = 14; working up X = 1.82). After 107 hours of operation at 210° a conversion rate of 40% was attained (Mv = 17; X = 1.73). Increasing the temperature of the first step to 223° failed to cause an increase in conversion rates or an improvement of the consumption ratio (U = 58; Mv = 23; X = 1.84). A further increase in temperature (229° first step; 226° second step; 222° third step) failed to cause a substantial improvement (U = 65; Mv = 23; X = 1.5). Each of the individual steps yields about the same conversion rate (U - 25 to 30%) and the same quantity of methane formed. The consumption ratio varied between X = 1.4 and 1.7. None of the steps was distinguished by any particular effect. After 286 hours of operation the experiment was terminated.

Assessment of the catalyst

In three steps at 220° a conversion rate of 60% could be attained with synthesis gas. (Rest illegible).

M. Beth

MB:hlm

SINCLAIR REFINING COMPANY

April 21, 1947

1659

S-1,2

Reel 42
Frame 353

Rees October 13, 1944

Experiment 808

This test is still running at this date. We are operating with the same catalyst as at experiment 807 (PN83). The procedure at the reduction with water-gas was studied in detail during the first 15 minutes by drawing samples every two minutes. The results are shown in the table which follows. After 60 minutes the pretreatment procedure was discontinued. The reactor was flushed with nitrogen and the temperature was reduced to 220°. After charging water gas samples were drawn. Up to 220° the conversion rates were low. However, at 230° the rates were already quite satisfactory. On putting through about 200 l/hr. per ltr of catalyst, the conversion rate was about 24% (Mv = 15; X = 0.89; A = 35). Without raising the temperature the conversion rates rose to 34% (Mv = 9; X = 0.90) within 18 hours of operation.

Thereby it is confirmed that at a space velocity of about 200 l/hr per ltr. of catalyst a consumption ratio of X = 0.9 can be attained. With a conversion rate of 30% a 10 m^3 converter would produce at least 2 tons/day. Because of this desirable result we shall continue the experiment for some time and perhaps feed synthesis gas for a short time.

We are actually running pretreatment tests in the laboratory convertors with catalyst containing only 10 parts of kieselgur at extremely low temperatures.

The latest analysis in regard to experiment 808 says: 230°C.; 49 hours of operation; through-put 230 l/hr per ltr. of catalyst; U = 29.7; Mv = 5; X = 0.84; A = 47.3.

Table Concerning Pretreatment

No. 752. Catalyst # PN83; Reactor capacity 1.6 ltr. experiment #808

Date Oct. 10, 1944

Per. of oper.		2"	4"	6"	8"	10"	13"	15"	20"	30"
Temp. °C.		250°	250°	250°	250°	250°	250°	250°	250°	250°
Vol. % CO_2	7.5	71.6	79.2	77.7	42.8	33.1	21.2	22.5	16.0	13.1
C_nH_m	0.0	0.3	0.0	0.1	0.1	0.2	0.3	0.1	0.3	0.1
O_2	0.0	0.1	0.0	0.0	0.1	0.2	0.3	0.1	0.0	0.1
CO	37.5	0.0	0.2	1.7	20.0	20.8	24.1	27.0	30.4	33.4
H_2	49.8	0.7	5.3	8.7	28.1	36.9	40.2	43.6	46.9	48.2
CH_4	0.2	0.8	0.4	0.5	0.5	0.6	0.3	0.2	0.8	0.5
Vol. % N_2	5.0	26.5	14.9	11.3	8.8	7.6	6.9	6.5	5.9	5.6

M. Beth

MB:hlm

1660

SINCLAIR REFINING COMPANY

S-13

Rees, October 10, 1944

Experiment 807

100 Fe, 5 Cu, 10 Ga O, 30 kgr (Solution of Caustic Soda Precipitation)

1% KOH Impregnation

Preparation of Catalyst PN 83 in the Catalyst Laboratory Rees

Hot nitrate solution (1.8 kg Fe and the corresponding Cu- and Ca- quantities in 80 l of water) are introduced into a boiling solution of caustic soda (4.1 kg NaOH in 46 l of water). Addition of 540 g of kieselguhr. After a short period of stirring filtration on the suction filter. Washing with 10 x 10 l of hot water - system water, and once more filtration on the suction filter. Processing of the catalyst cake with 540 cm^3 of caustic potash solution (18 g KOH) in the kneading maching for an hour. Spreading of the cake on trays. Drying in the drier at 120° for 16 hours. Forming into 3 mm granules.

Testing of the Catalyst in the 16-tube convertor.

1.6 l (0.82 kg) of unreduced contact is filled into the convertor. Drying of the catalyst with air (1500 l/h) at 250° for 12 hours. Flushing of the convertor with 100 l of nitrogen (30 minutes). Starting with water gas at 250° maintaining a constant quantity of exit gas of 150 l/h. - - After 12 minutes the first sample was drawn off. It showed that CO and Hg had been consumed in the ratio X = 1.08. The methane formation rate was practically zero. Most of the CO_2 formed is certainly generated by the reduction of the Fe_2O_3. It seems that the hydrogen, too, participates in the reduction. After 25 minutes the strong CO_2 formation was terminated. Normal synthesis conditions seem to prevail thereafter. Initially the conversion rates were low; however, after about 4 hours of operation a rate of 61% was attained (Mv = 20). The consumption ratio was favorable (X = 0.78). The gas through-put was about 1.35 to 1.4 times the ordinary rate. Thereafter the conversion rate showed a further increase to 65%; but then it decreased gradually, especially, after 30 hours of operation. After 46 hours of operation (V = 46; Mv = 28; X = 0.71) the experiment was terminated.

Evaluation of the Experiment.

The catalyst is reduced at 250°C with water gas within about two hours. CO_2 is thereby generated and probably hydrogen, too, is consumed. Then the formation of hydrocarbons is started, while the conversion rate is gradually rising. At 250° and on

putting through 1.4 times the normal quantity (140 l/ hr. per ltr. of catalyst) conversion rates up to 65% can be attained (Mv = 24; X = 0.77; A = 89). Thereafter, however, the output decreases gradually to 46%. The methane formation rate rises. Since this experiment was only aimed at studying more carefully the reduction phenomena, it was discontinued after 46 hours of operation.

MB:op

M. Beth

SINCLAIR REFINING COMPANY

1662

Ruhrchemie, A.G.
Oberhausen - Holten, June 13, 1944

S-14

State of the Fe - Catalyst Tests

1.) Once through, 10 atü; the potassium-water-glass impregnated catalyst turned out to be hard to reproduce (probably because of the unhomogeneous composition of the water glass and its containing traces of Na). That is why we are actually trying to replace the water glass by KOH or K_2CO_3. These contacts, too, gave a favorable result for X when pretreated with water glass. The methane values are still rather high for those contacts, as well as for the water-glass contacts. Up to this time no manner of pretreatment could eliminate these disadvantages. However, our project has not yet been exhausted. We continue our tests in the following directions: combined pretreatment with carbon dioxide, water glass and hydrogen at different temperatures, over varying periods of time, etc; impregnation with potassium hydroxide, potassium carbonate, etc.; reduction of the kieselguhr content to 10 kgr.-

2.) Recycle, 10 atü; the current test running with synthesis stock in the HR-reactor gives at 210° conversion rates of 70% and an X of 1.6. The methane formation rate is high (Mv = 18). Catalyst #F2093 goes on operating with good conversion rates, low methane rates and a favorable consumption ratio. We continue our efforts to reproduce this contact.

3.) Once through, ordinary pressure; the first test was discontinued after 500 hours (conversion rate U = 58; Mv = 14; X = 0.6). Actually a contact is operating in the HR reactor, which is also yielding a conversion rate of 60% after being reduced with hydrogen. In the near future we shall test a 10 kgr catalyst.

Assuming that in the course of time the Reichsamt-test went on showing the same low methane formation, we may figure that the CO_2-free water gas exercises an influence on the methane formation. I do not think that it is influenced by the construction of the reactor or by the manner of charging it.

(Rest of report not translated.)

SINCLAIR REFINING COMPANY

April 23, 1947 1663

S-15

Reel 42
Bag 3439 #22
Page 373

Oberhausen-Holten, September 26, 1944

Experiment 786

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation) potassium water-glass impregnation (0.45 K/100 Fe)

Preparation of catalyst #PN74

Hot nitrate solution (1.8 kg of Fe and the corresponding Cu and Ca quantities dissolved in 50 ltr. of water) are introduced into a boiling soda solution (6.4 kg. of soda in 50 ltr. of water). Adding of 540 g. of kieselgur. After a short period of stirring filtration on the suction filter. Washing with 10 times 10 ltrs. of hot condensate. Suspending in 100 ltr. of water and once more filtering on the suction filter. Treating the catalyst cake on the kneading machine for 30 minutes with 72 cm^3 of potassium water-glass solution which contained 342 g. of SiO_2, (111 g. of K/l and 21 g. Na/l, and had been diluted to 350 cm^3 before the impregnation. Spreading of the cake on trays. Drying in the drier at 110°. Forming into 1.5mm granules.

Testing of the catalyst in the 42 - tubes-reactor

Filling of 5.2 ltr. of non-reduced contact into the 42-tubes-reactor. Heating up with hot air while passing carbon dioxide. Preparation of the hot air: "Jaeger" blast apparatus 60 m^3/hr., oil heated tubular furnace 104 tubes of 12 mm I.D. and 3 m height, 14 m^2 heating surface, 50 ltr. capacity. After 5 hours a temperature of 250°C was attained. Through-put of water gas 1000 l/hr.

Temperatures:

In front of the reactor	253°
At top of the reactor	256°
At middle section of the reactor	257°
At bottom of the reactor	
Behind the reactor	236°

The temperature measurements were hard to carry out because of unfaverable placement of the indicating connections. After 16 hours of operation at 250° and 1000 ltr. through-put the conversion rate was 35%; the methane formation Mv = 21%; the consumption ratio X = 0.72; yields 51.3 g/m^3. On raising the temperature to 260° and reducing the through-put to 500 ltr., after 117 hours of operation the conversion rate amounted to 42% (Mv = 22; X = 0.7) and the 58 g/m^3. Because of an airplane attack the experiment had to be prematurely terminated.

Evaluation of the experiment

The reactor could be kept at a uniform temperature by means of hot air. The catalyst, without undergoing a prior reduction could have

Evaluation of the Catalyst.

Good activity, working-up ratio fair (X = 1.13) Methane form rate initially low, later higher (MW = 14).

M. Beth

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SINCLAIR REFINING COMPANY

April 24, 1947

1665

S-16

Reel 42
Bag 3439
Page 374

Oberhausen-Holten, September 21, 1944

Experiment 777

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation) 1% KOH impregnation

Preparation of catalyst #PN66

Introducing hot nitrate solution (1.8 kg Fe and the corresponding Cu and Ca quantities in 50 l. of water) into boiling soda solution (6.4 kg of soda in 50 l. of water). Adding 540 g. of kieselgur. After a short time of stirring, filtration on the suction filter. Washing with 10 x 10 ltr. of hot condensate. Suspending in 100 ltr. of water and once more filtering on the suction filter. Treating the catalyst cake with 540 cm^3 KOH solution (33 g. KOH/ltr.) in the kneading machine for 30 minutes. Spreading of the cake on trays. Drying in the drier at 110°. Forming into 3 mm granules.

Water-gas pretreatment

Filling 7 ltr. of "Gruenkorn" (non-reduced catalyst granules) into a 31-tubes-reactor (20 mm I.D. each tube, height 800 mm). Heating up to 250° in a slow CO_2 stream. Through-put of water gas (200 ltr./hr. per ltr. of catalyst) for 24 hrs. Cooling down in a slow water gas stream. Discharging under nitrogen into a flask filled with carbon dioxide.

Reduction value 55% (acetic-acid procedure)

Testing the catalyst in reactor MR7

Filling 2.88 kg. (ab. 5 ltr.) of pretreated catalyst into the reactor. Pressing one of 10 atü of water gas and heating up. Starting with 100° feed-stock through put (350 ltr./hr.) and gradual rise in temperature. At 202° after 35 hours of operation a conversion rate of 45% was attained (Mv = 6; X = 1.36). After 85 hours of operation the temperature was 214°C.; stock through-put 100 ltr./hr per ltr. of catalyst; conversion rate 55%; methane formation Mv = 12; working-up ratio X = 1.10. On keeping a temperature of 214° the through-put was increased. The effect of this procedure is shown in the following table.

brought in the reactor with water gas to a mean conversion rate of about 30% and 250° and with a double charge.

M. Beth

SINCLAIR REFINING COMPANY

April 24, 1947

Reel 42
Bag 3439-22
Page 375

1667

S-17

Oberhausen - Holten
September 21, 1944

Experiment 774

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation) 0.5% KOH-impregnation.

Preparation of the catalyst PN65 in the laboratory

Introducing hot nitrate solution (1.8 kg Fe and the corresponding Cu and Ca quantities in 50 ltr. of water) into a boiling soda solution (6.4 kg of soda in 50 ltr. of water). Addition of 540 g. of kieselgur. Stirring for a short period of time. Filtration on the suction filter. Washing with ten times 10 ltr. of hot condensate. Suspension of 100 ltr. of water and renewed filtering on the suction filter. Treating the catalyst cake with 540 cm^3 of KOH solution (16.7 g. KOH/l) in the kneading machine for 30 minutes. Spreading of the cake on trays. Drying in the drier at 110°. Forming into 3 mm granules.

Water gas pretreatment

Filling about 7 ltr. of catalyst into a 3l tubes reactor (each tube 20 mm I.D., height 800 mm). Heating up to 250° in a slow CO_2 stream. Through-put of water-gas (200 ltr./hr per ltr of catalyst) in 24 hours. Cooling down in a slow current of water. Discharging under nitrogen into a flask filled with CO_2. Reduction value: 38%.

Testing the catalyst in reactor MR6

Filling 2.91 kg (about 5 ltr) of pretreated catalyst into the reactor. Pressing on 10 atü of water gas and heating up. Starting with a temperature of 100°, feed-stock through-put (350 ltr./hr) and gradual raising of temperature. After 21 hours of operation at a temperature of 190° the conversion rate was U = 31% (Mv = 11; X = 1.50). In order to attain a conversion rate of 53%, the temperature had to be increased to 221°. The methane formation averaged Mv = 12, the consumption ratio X = 1.15. After 250 hours of operation the conversion rate decreased to 46% at 221° and the rate of methane formation increased.

Evaluation of the catalyst

Activity poor (221°, U = 53). Working-up ratio good (X = 1.15).

M. Beth

MB:hlm

SINCLAIR REFINING COMPANY

April 23, 1947 1668

Reel 42
Bag 5439-22
page 376

S-18

Oberhausen Holten
September 14, 1944

Experiment 747

100 Fe, 5 Cu, 10 CaO, 30 Kgr (soda precipitation) KOH impregnation (1.8 KOH/100 Fe)

Preparation of the catalyst #PN47 in the catalyst laboratory.
Confer experiment 735 (Reel 42, page 380).

Reduction in a glass tube (reactor chamber).
50 cm³ of "Grunkorn" (unreduced catalyst granules) are filled into a glass tube (15 mm I.D.). Length of the bed 310 mm. H_2N_2 (300 l./hr.) are made to pass over it at 300° for an hour. Cooling down in a slow H_2N_2 stream. Discharging into a flask filled with CO_2.
Reduction value: 60% (Acetic-acid method).

Testing of the catalyst in reactor HR8
2.65 kg of catalyst are charged into the reactor. Rapid heating up to 220° under water gas through put. After the first hours of operation the conversion rate was 50%. Without increasing the temperature it rose gradually to 58% (Mv = 14; X = 0.62). After 500 hours of operation the experiment was terminated.

Evaluation of the catalyst
The catalyst operating under ordinary pressure had a conversion rate of 56% at 220° for 500 hours of operation. The methane formation was Mv 14. The consumption ratio was X = 0.6.

M. Beth

MB:hlm

SINCLAIR REFINING COMPANY

1669

September 14, 1944

S-19

Experiment 736

100 Fe, 5 Cu, 10 CaO, 30 kgr (Soda Precipitation) Potassium - Water-Glass Impregnation (0.45 K/100 Fe)

Preparation of the Contact #PN43 in the Catalyst Laboratory.

Same method of preparation as PN32 (confer exp. 707) - Granulation 1.5 mm.

Water Gas Treatment: (reactors 7 and 2)

Filling 5 ltr of "Grünkorn" into reactor 7 and 2 ltr into reactor 2. Heating up to 250° in CO_2 atmosphere (16 hours reactor 7, 6 hours reactor 2). Water-gas through-put (issuing quantity: 100 ltr/hr per 1 of catalyst) for 48 hours. Gas analysis after 43 hrs.

CO_2:	7.2	29.6	R_3 (out of N_2): 0.722
SKW:	0.0	1.5	R_5 (calculated): 0.690
O_2:	0.1	0.1	
CO:	37.3	13.2	U = 54.2%
H_2:	50.2	45.0	Mv = 19.4%
CH_4:	0.0	3.4	X = 0.68%
N_2:	5.2	7.2	A = 79.6 g/m³

Cooling down in the water gas stream (20 l/l-catalyst) for 15 hours. Discharging under nitrogen in a flask filled with CO_2. Reduction value: 51% (Essugs - method); 24% (Hg Cl_2 - method); Fe - density: 310 g/l. Density: 545 g/l.

Testing the Contact in Reactor MR7.

Introducing 2.75 kg (ca. 5 l) catalyst into the reactor. Pressing on 40 atü water glass and heating up. Beginning with 100°C gas through-put (350 l/hr). After 36 hours of operation at 201° a conversion rate of 45% was attained, (Mv = 7; X = 1.21) On gradually increasing the temperature to 211°, after 108 hours of operation the conversion rate amounted to 59% (Mv = 8; X = 1.17) In order to keep this conversion rate constant, it was necessary to increase the temperture still more up to 221°. The average methane formation rate increased up to Mv = 12; whereas the consumption ratio remained around X = 1.12 and showed a slight decreasing tendency only towards the end of the experiment after 600 hours of operation. The experiment has been terminated after 800 hours of operation. The paraffin was of a yellow color.

1670

Through-put Nl water-gas per hr. per ltr. catalyst	Conversion rate U	Methane Formation My	Consumption ratio	Yields g/m^3 calculated	Yields Co/day with 10 m^3 catalyst
100	56	12	1.10	87	2.1
150	43	9	1.16	72	2.6
175	35	13	1.16	55	2.3
200	29	8	1.18	49	2.35
200	22	6	1.22	36	2.60

After 372 hours of operation the experiment was terminated because of the damages caused by an attack of bombers.

H. Beth

1671

SINCLAIR REFINING COMPANY

September 14, 1944

Experiment 735

S-20

100 Fe, 5 Cu, 10 CaO, 30 kgr (Soda Precipitation) KOH-Impregnation

(1.8 KOH/100 Fe)

Preparation of Catalyst #PN47 in the catalyst laboratory.

Hot nitrate solution (1.8 kg Fe and the corresponding Cu and Ca quantities in 50 ltr of water) are introduced into boiling soda solution (6.2 kg of soda in 50 ltr of water). Ph-value 8.8 to 9.0. Addition of 540g of kieselguhr. Stirring for a short period of time. Filtration by means of a suction filter. Washing with 100 l of water. Treatment with 370 cm^3 of KOH-solution (100g KOH/l) in the kneading machine during 30 minutes. Spreading on sheets. Drying in the drier at 110° during 12 hrs. Granulation to 15 mm.

Watergas Treatment (reactors 3 and 6).

5 ltr of "Grünkorn" are filled in reactor #6, and 2 ltr into reactor #3. Heating up to 250° in a CO_2 atmosphere (5 hrs). Through-put of water gas (issuing quantity: 100 l/hr per 1 catalyst) for 24 hours. Gas analysis after 18 hours.

CO_2	: 7.3	32.9	R (out of K)	: 0.768
SKW	: 0.1	1.7	R (Calcul. without K)	: 0.668
O_2	: 0.1	0.2	V = 57.4%	
CO	:37.5	10.1	Mv = 13.6%	
H_2	:50.0	46.1	X = 0.63	
CH_4	:00.0	2.5	A = 90.0	
N_2	: 5.0	6.5		

Cooling down in the water gas current (20 ltr/ltr of catalyst) for 15 hours. Discharging under nitrogen into a flask filled with CO_2. Testing of the catalyst in reactor MR4.

Circulation

Filling of 2.90 kg (about 5 ltr) into the reactor. Pressing on of 10 atü of water gas and heating up. Beginning with a temperature of 100°, through-put of the stock (350 ltr/hr). At 202° after 24 hours of operation the conversion rate was 42% (Mv = 3.2; X = 1.49). By increasing the temperature to 215°C., a conversion rate of 62% (Mv = 12; X = 1.24) was maintained for a considerable length of time. By increasing the temperature to 220° an output of 68% was obtained (Mv = 14; X = 1.2). The experiment was terminated after 740 hours of operation. The paraffin was of a light yellow color.

Evaluation of the Contact:

Activity sufficient: Methane formation rate high (Mv = 14). Consumption ratio good (X = 1.2) confer experiment 738.

MB:op

M. Beth

SINCLAIR REFINING COMPANY

April 24, 1947 1673

Reel 42
Bag 3439-22
Page 382

S-21

Oberhausen-Holten - September 11, 1944

Experiment 727

100 Fe, 5 Cu, 40 ZnO, 5 kgr (soda precipitation potassium water glass impregnation (0.45 K/100 Fe).

Preparation of catalyst PN45 in the laboratory

Same procedure as for PN32 (confer experiment 707, p. 394), however, CaO has been replaced by ZnO in the aforementioned ratio to Fe.

Reduction in the 6 ltr. reductor (R84)

Same conditions as in experiment 707.

Testing of the catalyst in the reactor MR6.

Filling of 4.26 kg. (about 5 ltr.) into the reactor. Pressing on of 10 atü water gas and heating up. Starting with 100°C. feed-stock through-put (300 ltr./hr.) slowly increasing the temperature. After 30 hours of operation at 200° the conversion rate was 40% (Mv = 14). At 215° a constant conversion rate of 62% (Mv = 20; X = 0.73) was achieved. The experiment was terminated after 300 hours of operation.

Evaluation of the catalyst

Activity good (215° - U = 62%). Methane formation rate high (Mv = 20). Working-up ratio fair (X = 0.73).

M. Beth

MB:hlm

SINCLAIR REFINING COMPANY

1674

April 24, 1947

Reel 42
Bag 3439-22
Page 382

S-22

Oberhausen-Holten
September 11, 1944

Experiment 729

100 Fe, 5 Cu, 30 ZnO, 5 kgr (soda precipitation) 0.45% K/100 Fe potassium water glass impregnation

Preparation of the catalyst #PN44 in the laboratory

Same preparation as #PN32 (confer experiment 707, p. 394), CaO, however, has been replaced by ZnO in the aforementioned ratio to Fe.

Reduction in the 6 ltr. reductor - R85

Same conditions as in experiment 707
Withering: 27%

Testing the catalyst in the reactor MR8

Filling 4.18 kg (about 5 ltr) of catalyst into the reactor. Pressing on 10 atü of water gas and heating up. Starting with a temperature of 100° stock is put through while slowly raising the temperature. At 200° after 35 hours of operation the conversion rate was 40% (Mv = 13). At 213° a constant conversion rate of 63% was achieved. The methane formation averaged Mv = 16, consumption ratio X = 0.75. The experiment was terminated after 320 hours of operation.

Evaluation of the catalyst

Activity good (213° : U = 63%). Methane formation rate high (Mv = 16). Working-up ratio fair (X = 0.75).

M. Beth

SINCLAIR REFINING COMPANY

April 24, 1947

S-23

Oberhausen-Holten, September 11, 1944

Experiment 726

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation) potassium water glass impregnation (0.45 K/100 Fe).

Preparation of catalyst PN43 in the laboratory
Same procedure as for PN32 (confer experiment 707, p. 394).

Reduction in the glass tube (reductor chamber)
Same conditions as in experiment 721

Testing the contact in reactor MR4
Filling 2.5 kg (ca 5 l) of catalyst into the oven. Pressing on 10 atü of water gas and heating up. Starting with 100° C., feed-stock through-put (350 ltr./hr.) and further slow temperature increase. After 35 hours of operation at 200° the conversion rate was U = 32% (Mv = 13; X = 1.18). By increasing the temperature very gradually furtheron at 205° C after 83 hours of operation the conversion rate attained U = 44% (Mv = 16; X = 0.93). After 227 hours of operation at 214° a conversion rate of U = 58% (Mv = 21; X = 0.93) was attained. Because of excessive methane formation and because of the consumption ratio deteriorating in correlation therewith, the experiment was discontinued at 214° after 251 hours of operation.

Evaluation of the catalyst
Conversion rate satisfactory (214°: 58%); consumption ratio favorable (X = 0.93); methane formation on high (Mv = 22).

M. Beth

SINCLAIR REFINING COMPANY 1676

April 24, 1947

Reel 42
Bag 3439
Page 384

S-24

Oberhausen-Holten, September 11, 1944

Experiment 724

100 Fe, 5 Cu, 10 CaO, 10 kgr (soda precipitation) potassium water glass impregnation (0.45 kg/100 Fe)

Preparation of the catalyst FN43 in the laboratory
Same procedure as for FN32 (confer exper. 707, page 394)

Reduction in the glass tube (reactor chamber)
Preparation in individual charges of 50 cm^3 each. Filling 50 cm^3 of "Gruenkovn" (non-reduced granules) into a glass tube (15 mm I.D.). Length of layer 310 mm. Passing H_2N_2 (300 ltr./hr.) at 250° for one hour. Cooling down in a slow H_2N_2 stream. Discharging into a flask filled with CO_2.

Testing the catalyst in reactor MR7
Filling 2.16 kg of catalyst (about 5 l) into the reactor. Soaking it with cetane. Pressing on 10 atü of water gas and heating up. Starting with 190°C. feed-stock is put through (400 l/hr.). After 28 hours of operation at 210° the conversion rate was 33% (Mv = 15, X = 0.95). In spite of a gradual increase in temperature to 220°, the conversion rate could not be raised above 45%. The methane formation averaged Mv = 20, the working-up ratio X = 0.85. The experiment was terminated after 264 hours of operation.

Evaluation of the catalyst
Very poor activity (220° : U = 45; methane formation high (Mv = 20). Working-up ratio poor (X = 0.85).

M. Beth

April 24, 1947

S-25

Reel 42
Bag 3439-22
Page 385

Oberhausen-Holten, September 11, 1944

Experiment 723

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation) potassium water glass impregnation (0.9 K/100 Fe)

Preparation of the catalyst PN40 in the laboratory

Same procedure as for PN32, (confer exper. 707, page 394) however, stronger potassium water glass impregnation (140 cm^3 potassium water glass solution (342 g. SiO_2/l) diluted with water to 350 cm^3).

Reduction in the 6 ltr. reductor (R82)

Filling 6.2 liter of "Gruenkovn" into the nitrogen-charged apparatus. Passing of H_2N_2 at 242-253° (35 m^3/hr) for an hour. Flushing the apparatus with nitrogen. Taking out the trough. Cooling down with a H_2N_2 blast. Discharging under nitrogen. Reduction value: 67% (Acetic acid method).

Testing the catalyst in the reactor MR8

2.71 kg (about 5 l) of catalyst are filled into the reactor and soaked with cetane. 10 atü of water gas are pressed on and heated up. Beginning with 190° feed-stock is put through (400 l/hr.). After 31 hours of operation at 211° U = 37 (Mv = 12; X = 0.77). Soon thereafter the methane formation rate increased (Mv = 46), thereupon the conversion rate decreased. After 120 hours of operation the experiments were discontinued at 211°.

Evaluation of the catalyst

Conversion rate poor; strong inclination to form methane; consumption ratio unsatisfactory (X = 0.75).

M. Beth

MB:hlm

SINCLAIR REFINING COMPANY

April 24, 1947

S-26

Oberhausen-Holten, September 11, 1944

Experiment 722

100 Fe, 5 Cu, 10 CaO, 50 kgr (soda precipitation) potassium water-glass impregnation (0.45 K/100 Fe).

Preparation of catalyst PN42 in the laboratory

Same procedure as for PN32 (confer. exper. 707; page 394) however, addition of a larger kieselgur quantity (900 g).

Reduction in the 6-ltr. reductor (R81)

Same conditions as in experiment 707.

Testing the catalyst in the reactor MR4

2.25 kg (about 5 l) of catalyst was filled into the reactor and soaked with cetane. Pressing on of 10 atü of water gas and heating up. Starting with 190°, feed stock is put through (400 l/hr.) and the temperature is raised gradually. After 44 hours of operation at 214° a conversion rate of 53% was attained (Mv = 14; X = 0.98). On raising the temperature for 1°, strong methane formation occured (Mv = 73). Soon thereafter, the conversion rate was reduced to 40%. The experiment was discontinued after 68 hours of operation.

Evaluation of the catalyst

Strong inclination towards methane formation. Consumption ratio favorable (X = 1.0).

M. Both

MB:hlm

SINCLAIR REFINING COMPANY

April 24, 1947 1679

Reel 42
Bag 3439-22
Page 387

S-27

Oberhausen-Holten, September 11, 1944

Experiment 721

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation) potassium water-glass impregnation (0.9 K/100 Fe.

Preparation of the catalyst FN40 in the laboratory

Same procedure as for FN32 (confer exp. 707, p. 394) however, stronger potassium water-glass impregnation (342 SiO_2/l diluted with water to 350 cm^3).

Reduction in the glass tube (reductor chamber).

Preparation in individual charges of 50 cm^3 each. Filling 50 cm of "Grünkorn" into a glass tube (15 mm I.D.). Length of layer 310 mm. Passing H_2 (300 l/hr) at 300° for one hour. Cooling down in a slow H_2 stream. Discharging into a CO_2 filled flask. Reduction value 62% (acetic-acid method) 16.3% (Hg method).

Testing the catalyst in reactor KR11

2.32 kg of catalyst (about 5 l) are filled into the reactor and and soaked with 3 l. of cetane. 10 atü water gas are pressed on. Heating up. Starting with 190° feed-stock is put through (400 l/hr). After 36 hours of operation at 211° the conversion rate was 45% (Mv = 7; X = 0.05). By cautiously raising the temperature to 220° the conversion rate increased to 59% (Mv = 19; X = 0.79). The experiment was terminated after 396 hours of operation at 221°.

Evaluation of the catalyst

Methane formation too high (Mv = 19). Working-up ratio unsatisfactory (X = 0.79). Conversion rate satisfactory 220°; U = 59%.

M. Beth

SINCLAIR REFINING COMPANY 1680

April 24, 1947

Reel 42
Bag 3439-22
Page 389

S-28

Oberhausen-Holten
September 11, 1944

Experiment 719

100 Fe, 5 Cu, 10 CaO, 50 kgr † (soda precipitation) potassium water-glass impregnation (0.9 K/100 Fe)

Preparation of catalyst PN39 in the laboratory

Same procedure as with PN32 (confer. exper. 707, page 394), however, stronger potassium impregnation (140 cm^3 potassium water-glass solution (342 g. of SiO_2/ltr. diluted with water to give 350 cm^3), and addition of a larger quantity of kieselgur (900 g.).

Reduction in the 6 ltr. reductor (K-79)

Same conditions as with experiment 707.

Testing the catalyst in the reactor KR10

2.07 kg (about 5 l) of catalyst are filled into the reactor and soaked with cetane. 10 atü of water gas are pressed on. Heating up. Starting with 190°, feed-stock is put through (300 l/hr.). Within two hours temperature rises to 195°; after 4 hours of operation200°-After 19 hours of operation 209° the conversion rate measured was 35%. The working-up ratio was at X = 1.0. The initially low methane formation rate rose at 215° to Mv = 19. In spite of our raising the temperature to 220°, the conversion rate attained only 42%. The methane formation amounted to Mv = 20. The consumption ratio averaged X = 1.0. The experiment was terminated after 113 hours of operation at 220°C.

Evaluation of the contact

Conversion rate poor (220°; U = 40); methane formation high (Mv = 20); consumption ratio favorable (X = 1.0).

M. Beth

† The analysis of the "Gruenkorn" showed:
100 Fe, 3.82 Cu, 3.9 CaO, 43 kgr.

SINCLAIR REFINING COMPANY

April 24, 1947

1681

Reel 42
Bag 3439-22
Page 390

S-29

Oberhausen-Holten
September 11, 1944

Experiment 718

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation) potassium water-glass impregnation (1.8 K/100 Fe)

Preparation of the catalyst PN41 in the laboratory

Same procedure as with PN82 (confer exper. 707, page 394); however, stronger potassium water-glass impregnation (280 cm^3 potassium water-glass solution (342 g. of SiO_2/ltr) diluted with water to give 350 cm^3).

Reduction of the catalyst in the 6 ltr reductor (R78)

Same conditions as with exper 707. Shrinking: 17%.

Testing the catalyst in reactor MR9

2.42 kg (about 5 ltr.) of catalyst are filled into the reactor and soaked with 3 ltr. of ceptane. 10 atü of water gas are pressed on. Heating up. Starting when the temperature reaches 190°, feed stock is put through (400 ltr/hr). Rather rapid temperature increase. After 19 hours of operation the temperature was 210° and the conversion rate 37% (Mv = 13, X = 0.8). For attaining a conversion rate of 55%, a temperature of 222° was necessary. At this rate of conversion, the methane formation averaged Mv = 12, the consumption ratio X = 0.7. The experiment was terminated after 260 hours of operation at 224°.

Evaluation of the catalyst

Rate of conversion low (220° : U = 55%); methane formation excessive (Mv = 12) - pure white paraffin.

M. Beth

MB:hlm

SINCLAIR REFINING COMPANY

April 24, 1947 1682

Reel 42
Bag 3439-22
Page 391

S-30

Oberhausen-Holten
September 11, 1944

Experiment 717

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation) potassium[x] water-glass impregnation (0.9 K/100 Fe)

Preparation of catalyst PN40 in the laboratory

Same procedure as with PN32 (confer experiment 707); however, stronger potassium water-glass impregnation (140 cm^3 of potassium water glass solution (342 g. of SiO_2/l), diluted with water to give 350 cm^3).

Reduction in the 6 ltr. reductor (R77)

Same conditions as with experiment 707.

Testing the contact in the reactor MR7

2.41 kg (about 5 l) of catalyst are filled into the reactor and soaked with cetane. 10 atü of water gas are pressed on. Heating up. When a temperature of 190° is reached feed-stock is put through (350-400 l/hr) and the temperature increased still further. Already at rather low temperatures high methane formation rates (205° : U = 32, Mv = 15; X = 0.95). By increasing the temperature to 215° the conversion rate could be raised to U = 52. The methane formation rate continued to be high (Mv = 20). The working-up ratio was about X = 0.9. Since the strong methane formation made it unfeasible to increase the temperature still further, the experiment was terminated after 139 hours of operation.

Evaluation of the catalyst

Methane formation excessive. Working-up ratio favorable. (X = 0.9).

M. Beth

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[x] The potassium water glass was composed as follows: 342 g. of SiO_2/l, 111 g. of K/l; 21 g. of Na/l.

SINCLAIR REFINING COMPANY

April 24, 1947 1683

9-31

Reel 42
Bag 3439-22
Page 392

Oberhausen-Holten, September 11, 1944

Experiment 715

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation) potassium water-glass impregnation (0.4 K/100 Fe)

Preparation of contact PN32 in the laboratory
Confer experiment 707, page 394.

Reduction in the 6 ltr reductor (R75)
Same conditions as with R74 (exp. 714). Reduction on value 62% (Acetic acid method).

Testing the catalyst in reactor MR3
Recirculation
2.45 kg (about 5 l) of catalyst are filled into the reactor and soaked with cetane. 10 atü of water gas are pressed on and heated up. When 190° are attained feed-stock is put through (500 l input, 1500 l recirculation) and the temperature is quickly raised to 195°C. (U = 35; Mv = 23; X = 1.3). At 200° after 24 hours of operation a conversion rate of 40% (Mv = 12 and X = 1.33) was attained. At 205° the conversion rate rose to 55% (Mv = 17%, X = 1.34). After 48 hours of operation at 210° the conversion rate rate was 62% (Mv = 18; X = 1.3). When the recirculation compressor failed, the experiment was changed over to the once-through process for a short time. Thereby heavy methane formation occurred (Mv = 80). After switching back to recirculation the methane formation gradually decreased. After rising the temperature to 215°, a conversion rate of 70% (Mv = 22 and X = 1.22) was attained. Because of the heavy methane formation the experiment was terminated after 177 hours of operation.

Evaluation of the catalyst
On recirculation, already at low temperatures heavy methane formation is observed. Conversion rate good. Working-up ratio outstanding (X = 1.22). Methane values excessive (Mv = 22).

M. Beth

SINCLAIR REFINING COMPANY

April 24, 1947 1684

Reel 42
Bag 3439-22
Page 393

S-32

Oberhausen - Holten
September 9, 1944

Experiment 714

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation) potassium water-glass impregnation (0.4 K/100 Fe)

Preparation of catalyst PN32 in the laboratory
Confer exp. 707

Reduction in the 6 ltr. reductor (R74)
6.2 l of "Gruenkorn" is filled into the nitrogen-charged atmosphere. 35 m^3 of H_2N_2 is passed at 288-302° for one hour. Flushing of apparatus with nitrogen. Taking out the trough. Cooling down with H_2N_2. Discharging with nitrogen.

Testing the contact in the reactor NR4
2.58 kg (about 5 l) of catalyst is filled into the reactor and soaked with 3 l of cetane. Pressing on of 10 atü of water gas and heating up. Starting with 190°, feed stock is put through (300-350 l/hr) and the temperature is increased to 195° within 4 hours (U = 30; Mv = 10; X = 1.0). After 24 hours of operation the temperature was raised to 200° within two hours (feed-stock through 350/l/hr.). The conversion rate did not rise but the methane formation rate rose to Mv = 20, the consumption ratio remained constant at 1.05. Even by a further increase in temperature to 210° the conversion rate could be brought only to 43% (Mv = 22, X = 1.0). On raising the temperature to 210°, heavy methane formation occurred (Mv = 75) so that the temperature was again reduced to 210° without delay. After 188° hours of operation at 212°C the conversion rate was 40% (Mv = 22 and X = 1.0). The discharging operation offered no difficulties.

Evaluation of the catalyst

Good working-up ratio (X = 1.0) however, excessive tendency towards methane formation. Slight rate of conversion (210°, U = 40; Mv = 20; X = 1.0).

M. Beth

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1660

S-33

Oberhausen-Holten
June 8, 1944

Experiment 725

100 Fe, 5 Cu, 100 CaO, SiO_2 (Soda Precipitation) Potassium water glass Treatment Pursuant to Lurgi.

Preparation of the catalyst PN37 in the laboratory.

Hot nitrate solution (1.8 kg Fe and the corresponding Cu and Ca-quantities in 50 l of water) is introduced into a boiling soda solution (6.4 kg of soda in 50 l of water). Filtration on the suction filter. Washing with 72 l of hot condensate. Suspension of the catalyst cake in a potassium water-glass solution (50 l of water + 443 cm^3 of a potassium water-glass solution, which contained 234g of SiO_2 per liter) and filtering in the suction filter. Spreading of the cake on trays. Drying in the laboratory at 110°. Forming 3mm granules.

Reduction in the 6-ltr-reductor (R83)

6.2 ltr of "Gruenkorn" are filled into the nitrogen charged apparatus. H_2N_2 is passed through at 300-310° for one hour (about 35 m^3/hr). Taking out the trough under nitrogen. Cooling down while passing H_2N_2. Discharging under nitrogen. Shrinking 35.5%.

Testing the catalyst in the reactor MR10

4.05 kg (about 5 l) of catalyst are filled into the reactor. 10 atü of water gas are pressed on. Heating up. When the temperature has reached 100°, feed stock is put (350 l/hr) through, and the temperature is slowly raised. After 55 hours of operation the temperature was 200° and the conversion rate 42% (Mv = 10; X = 0.8). At 214° after 223 hours of operation a constant conversion rate of 62% was attained. The methane formation averaged Mv = 16. The working-up ratio was about X = 0.73. The experiment was discontinued at 214° after 463 hours of operation, since the properties of the catalyst seemed to be established

Evaluation of the catalyst.

Activity good (214°: V = 62); methane formation rate high (Mv = 16); consumption ratio X = 0.71.

MB:op

M. Both

SINCLAIR REFINING COMPANY

April 24, 1947

1686

Reel 42
Bag 3439-22
Page 394

Oberhausen - Holten
September 11, 1944

S-34

Experiment 712

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation) potassium waterglass impregnation (0.4 K/100 Fe)

Preparation of catalyst PN36 in the laboratory
Confer experiment 707 (PN32)

Reduction in the 6 ltr. reductor (R72)
6 l. of "Gruenkorn" are filled into the nitrogen-charged apparatus. 35 m^3 of H_2N_2 are passed at 300° for 1 hr. Flushing the apparatus with nitrogen. Taking out the trough. Cooling down the catalyst with H_2N_2. Discharging under nitrogen. Shrinking 13%; reduction value 71% (acetic acid method).

Testing the catalyst in reactor MR9
2.45 kg (about 5 l) of catalyst are filled into the reactor and soaked with 3 l cetane. 10 atü water gas is pressed on and heated up. At reaching 170°, feed stock is put through (400 ltr/hr.) and the temperature increased to 200° within the next 12 hours. At 203° a conversion rate of 40% was measured (Mv = 10, X = 1.17). By means of a gradual increase in temperature to 212° no substantial increase in the conversion rate could be obtained. (212°: U = 44; Mv = 20, X = 1.05). At 214° after 75 hours of operation much methane was formed (Mv = 72). Thereafter, 45% was the maximum conversion rate attained, although the temperature was gradually increased to 223°. The methane formation was considerable (Mv = 20), the working-up ratio good (X = 1.0).

Evaluation of the catalyst
Low conversion rates (223° = 45%; methane formation excessive (Mv = 20); working-up ratio good (X = 1.0). Tendency to form much methane.

M. Beth

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1687

Oberhausen-Holten
June 8, 1944

S-35

Experiment 713

100 Fe, 5 Cu, 10 CaO, 30 kgr (Soda Precipitation) 3% K_2CO_3 Impregnation

Same preparation as PN31 (confer Exp. 709)

Reduction in the 6-ltr-reactor (R73)

6 l of "Gruenkorn" are filtered into the nitrogen-charged apparatus. 35 m^3 of H_2N_2 is passed through at 297-304° during an hour. Flushing with nitrogen. Taking out the trough. Cooling down the catalyst with H_2N_2. Discharging with nitrogen. Shrinking 17%; reduction value 63% (Acetic acid method).

Pretreatment of the reduced catalyst with water gas in reactor MR6.

2.67 kg of catalyst are filled into the reactor. CO_2-free water gas (15 l/hr) is passed through and heated up to 140°. At this temperature the catalyst was treated for 240 hours, maintaining a charge of 15 ltr/hr. In the exit gas 6-7% of CO_2 were found. The conversion rate was about 20%.

Testing the catalyst in the reactor MR6.

10 atü of water gas are pressed on and stock is fed at 340-400 l/hr. After increasing the temperature to 218° a conversion rate of 62% was attained (Mv = 15; X = 0.7). Since the experiment seemed no more interesting it was terminated.)

Evaluation of the Catalyst.

Conversion rate at 218° fair (V = 60); methane formation high (Mv = 15); working-up ratio X = 0.7.

Confer experiments 709 and 710.

M. Beth

MB:op

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1688

S-36

Oberhausen-Holten
June 8, 1944

Experiment 710

100 Fe,5 Cu,10 CaO,30 kgr (Soda Precipitation)3% K_2CO_3 Impregnation

Preparation of catalyst PN31 in the laboratory.

Confer experiment 709.

Reduction in the 6 ltr reductor (R 70)

Description confer experiment 709. Reduction value 78% (Acetic acid method).

Pretreatment of the reduced catalyst in the reactor MR8.

2.17 kg of catalyst are filled into the reactor under nitrogen. Carbon-dioxide-free water gas is passed through (50 ltr/hr) and heated up to 140°C (7 hrs). Through-put increased to 300 l/hr under raising the temperature to 150°. In the exit gas about 1% of carbon dioxide was found. After 90 hrs termination of the pretreatment.

Testing of the catalyst in reactor MR8.

10 atü of water gas are pressed on. At a through-put of 350-400 l/hr, the temperature is gradually raised. At 205° a conversion rate of 35% was attained (Mv = 15; X = 0.74). By slowly raising the temperature to 221° the conversion rate could be raised to 60% (Mv = 17). The paraffin formed was of a light yellow color. The experiment was terminated after 524 hours (including pretreatment).

Evaluation of catalyst.

Conversion rate at 221° good (V = 60); methane formation high (Mv = 17); working up ratio (X = 0.7).

M. Both

MB:op

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Oberhausen-Holten
June 8, 1944

S-37

Experiment 709

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation)* 3% K_2CO_3 Impregnation

Preparation of the catalyst PM31 in the catalyst.

Hot nitrate solution (1.8 kg Fe and the corresponding quantities of Cu and Ca in 50 l of water) is introduced in boiling soda solution (6.4 kg of soda in 50 l of water). Adding 540g of kieselguhr. After a short time of stirring, filtration on the suction filter. Washing with 10 x 10 l of condensate. Suspension of the homogenized catalyst cake in 100 l of water and once more filtering in the suction filter. Treatment of the catalyst cake with 572 cm^3 of potash solution (95g K_2CO_3/l) in the kneading machine for 30 minutes. Spreading the cake on trays. Drying in the drier at 110° for 16 hours. Pressing thru a 3 mm mesh.

Reduction in the 6-ltr-reductor (R69)

6 l of "Gruenkorn" (Unreduced catalyst granules) are introduced into the nitrogen charged apparatus and soaked with cetane. H_2N_2 is passed through at 100° during one hour (35 m^3). Flushing the apparatus with nitrogen. Taking out the trough and cooling it in the H_2N_2. stream. Discharging under nitrogen. Shrinking 14%; reduction value 75% (Acetic acid method).

Testing the catalyst in reactor MR5.

2.6 kg (5 l) of catalyst are filled into the reactor and soaked with cetane. 10 atü of water gas are pressed on and heated up. When 150° is reached, feed stock is put through and the temperature is raised once more.. At 200° after 11 hours of operation a conversion rate of 43% was attained (Mv = 8; X = 0.85). In order to attain a constant conversion rate of 62%, the temperature had to be gradually raised to 221°. From the 137th to the 1113th hour of operation an average conversion rate of 60% could be maintained (Mv = 20; X = 0.73). The experiment was only terminated, because the reactor was needed for something. No decrease in the conversion rate was to be observed during the last stage of the experiment. The discharging offered no difficulties.

Evaluation of the catalyst.

Activity good and constant (220°; V = 60% for 1000 hours of operation); methane formation high, but not injurious to the catalyst (Mv = 20). No tendency to excessive methane formation. Consumption rate X = 0.75.

* Accurate analysis of the unreduced catalyst showed, 100 Fe, 3.04 Cu, 8.1 CaO, 35.4 kgr.

M. Beth

MB:op

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1690

Oberhausen-Holten
June 8, 1944

S-38

Experiment 704

100 Fe,5 Cu,10 CaO,30 kgr (Soda Precipitation)3% KOH Impregnation.

Preparation of catalyst F2093 in the laboratory.

Description confer Exp. 696.

Reduction in the 6-ltr-reductor (R66)

6 l of "Gruenkorn" are introduced into the nitrogen-charged apparatus. H_2N_2 is passed through at 325° for three hours. Flushing of the apparatus with nitrogen. Cooling the trough with H_2N_2. Discharging under nitrogen. Shrinking 53%.

Pretreatment of the reduced catalyst with water gas in reactor MR 10.

3.67 kg of contact are filled into the reactor under a nitrogen atmosphere. Carbon-dioxide-free water gas is passed through (50 l/hr) and heated up to 110° (8 hrs). Increasing the through-put to 300 l/hr and then gradually raising the temperature, while accurately measuring the carbon dioxide formation. After reaching 130° (7 hrs) 300 l/hr of water gas (0.7% CO_2) are passed through for 63 hours. During the whole period of pretreatment, the carbon dioxide rate remains low; at the aforementioned through-put rate it averaged 2.4-1.5 l/hr of CO_2. The analyses of the gas showed that only CO and no H_2 was consumed. During the last pretreatment hours no more carbon dioxide was formed.

Testing of the catalyst in reactor MR10.

Pressing on of 10 atü of water gas and through-put of 340-400 ltr/hr. Gradual increase in temperature. At 210° a conversion rate of 60% was attained (Mv = 15; X = 0.75). Because of various failures in our operation, the temperature must be raised to 222° in order to obtain a mean conversion rate of 55%. The methane formation averaged about Mv = 12. The working-up ratio X = 0.72.

Evaluation of the catalyst.

Good initial activity (210°:V = 60); catalystnot very stable; at 222° only 55% conversion rate (Mv = 12; X = 0.72).

Confer Exp. 696, 697, 700, 595 and 720.

(Only Exp. 700 is included in Reel 42)

MB:op

M. Beth

SINCLAIR REFINING COMPANY

September 11, 1944

1691

3-39

Experiment #707

100 Fe, 5 Cu, 10 CaO, 30 kgr (Soda Precipitation) Potassium - Water-Glass Impregnation (0.4 K/100 Fe*).

Preparation of Catalyst #PN32 in the catalyst laboratory.

Hot nitrate solution (1.8 kg Fe and the corresponding Cu- and Ca- quantities into 50 l of water) is poured into a boiling soda solution (6.4 kg of soda in 50 l of water). 540 g of kieselguhr are added. Stirring for a short time. Filtration in a suction filter. Washing with 10 times 10 l of hot condensate. Suspension in 100 l of water and once more filtration in a suction filter. Reacting the catalyst cake with 70 cm^3 of potassium water glass solution, which contained 234 g of SiO_2/l pursuant to its analysis, and had been diluted to 350 cm^3 before being impregnated; kneading it in the kneading machine for 30 minutes; spreading the cake on sheets; drying it in the dryer at 100°C for 16 hours; forcing it through a 3 mm screen.

Reduction in the 6 l Reductor (R 67)

6.2 l of catalyst are fed into the nitrogen filled apparatus. H_2N_2 is passed through at 300°C during one hour (35 m^3). The trough is taken out under nitrogen. Cooling on passing H_2N_2. Discharging under nitrogen. Withering 15%; reduction value 81%.

Testing of the Catalyst in the Reactor MR 5.

Introducing 2,635 kg of catalyst into the reactor. Pressing on 10-atü water gas and heating up. On attaining 100°C, a gas-through-put of 350 lt/hr. At 200° a conversion rate of 30% was reached. The methane formation was Mv = 14. The working-up rate was approximately X = 1.1. The test had to be terminated because of technical difficulties.

Evaluation of the Contact.

Inhowfar the catalyst could be tested (66 hours of operation at 208°C) it showed a fair consumption ratio (X = 1.1). The methane formation ratio was rather high (Mv = 14).

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* No quantative K - analysis of the potassium water-glass employed has been made. We may assume the K-content to be about 110 g K/l.

MB:op
4-24-47

M. Beth

SINCLAIR REFINING COMPANY 1692

Oberhausen-Holten
June 8, 1944

9-40

Experiment 702

100 Fe, 5 Cu, 10 CaO, 30 kgr (Soda Precipitation) 3% KOH Impregnation

Preparation of Catalyst PN13 in the laboratory.

55g of kieselguhr are reacted in boiling soda solution (5.4 kg of soda, 50.4 l of water) for one minute. Hot nitrate solution (5 l with 1.8 kg of Fe and the corresponding quantities of Cu and Ca) are introduced. Introducing 485g of kgr. Stirring for a short period of time and filtering on the suction filter. Sucking off the mother liquor. Washing with 44 l of hot condensate. Treating the catalyst cake which has been dried by suction with 540 cm^3 of potassium liquor (100g KOH/l) in the kneading machine for 30 minutes. Spreading of the cake on trays. Drying in the drier at 120-140°; pressing through a 4 mm screen.

Reduction in the 6-ltr-reductor (R65)

6 l of "Gruenkorn" are filled into the heated nitrogen-filled apparatus. 35 m^3 H_2N_2 are passed through at 315-334°C for an hour. Taking out the trough and nitrogen, cooling in the H_2N_2 stream, discharging under nitrogen. Shrinking 13.3%. Reduction value 75% (Acetic-aaid process).

Pretreatment of the reduced catalyst with water gas in reactor MR11.

265 kg of reduced catalyst are filled into the reactor under nitrogen. Flushing with CO_2-free water gas. Pressing on 10 atü of water gas and heating up to 100° while passing through 50 l of CO_2-free water gas per hour. When a temperature of 100° is reached, the through-put is enhanced to 300/l/hr and the temperature is increased to 163° within seven hours. In the exit gas 4% CO_2. Beginning with the 9th hour of operation the operation goes on without pressure at 155° with CO_2-free water gas. In the exit-gas 0.8% CO_2. After 100 hours of operation the pretreatment is terminated.

Testing the contact in the reactor MR11.

Pressing on 10 atü of water gas and putting through 350-400 l/hr. Gradual increase in temperature. At 216° a conversion rate of 62% was reached (Mv = 12; X = 0.65). This conversion rate could be maintained on gradually increasing the temperature to 220°. In the last stage, the methane formation rate reached Mv = 20.

Evaluation of the catalyst.

In comparison with the not-pretreated catalyst PH4 (Experiment 676) the pretreated catalyst has a better activity. The methane formation rate is still too high. The consumption rate is poor.

SINCLAIR REFINING COMPANY

1694

Oberhausen-Holten
June 8, 1944

S-41

Experiment 700

100 Fe, 5 Cu, 10 CaO, 30 kgr (Soda Precipitation) 3% KOH Impregnation

Preparation of the catalyst F-2093 in the laboratory.

Confer experiment 696.

Reduction in the 6-ltr-reductor (R64)

Confer experiment 696.
Reduction value 63% (Acetic-acid method).

Testing the catalyst in the reactor KR6.

3.2 kg (about 5 ltr) of catalyst are filled into the reactor. Pressing on 10 atü of water gas and heating up. Starting with 150° feed-stock through put (350-400 l/hr) and further gradual temperature increase. Initially only slight methane formation (up to 220° averaging Mv = 5). Only at 223° a conversion rate of 55% was attained (Mv = 11, X = 0.72). After some time the conversion rate decreases to 50%, the methane formation decreases to Mv = 8 and the working-up ratio rises. Since the basic properties of the catalyst could be considered as established, the results premitting a comparison with experiment 696 and 697, the test was discontinued.

Evaluation of the catalyst.

Slight activity (223°; V = 55; Mv = 11; X = 0.72).
Confer Experiments 696, 697, 701, 705, 720.

SINCLAIR REFINING COMPANY

1695

S-42

Oberhausen-Holten
April 15, 1944

Experiment 690

100 Fe, 5 Cu, 10 CaO, 15 kgr (Soda Precipitation) 3% K_2CO_3 Impregnation

Preparation of the catalyst PN17 in the laboratory.

135g of kgr are reacted in boiling soda solution (6.4 kg of soda, 50 l of water) for one minute. Nitrate solution is added (1.8 kg of Fe and the corresponding quantities of Cu and Ca in 50 l of water). 135g of kgr are added. After stirring for a short period of time, filtration on the suction filter. Sucking off of the mother liquor. Washing with 44 l of hot condensate. Treating the catalyst cake which has been such dry with 540 mm^3 of potash solution (100 g/l) in the kneading machine for 30 min. Spreading of the cake on trays. Drying in the drier at 120-140°. Pressing through a 4 mm screen.

Reduction in the 6 ltr reductor (R60)

6 l of "Gruenkorn" are filled into the nitrogen-charged apparatus. 23 m^3 H_2N_2 at 250° are put through for 40 min. Cooling down in the N_2 stream. Discharging into a CO_2 filled flask and saturating with CO_2. Shrinking 17%; reduction value 59% (acetic acid method).

Testing the catalyst in reactor MR11.

3.14 kg (about 5 l) of catalyst are filled into the reactor. 10 atü of water gas are pressed on and heated up. Starting with 150° feed stock is put through (400-450 l/hr) and the temperature gradually increased still more. At 220° a conversion rate of 55% (Nv = 10) was attained. When the conversion rate decreased in spite of increasing the temperature the test was terminated. It was not particularly difficult to discharge the catalyst but the granules seemed to have crumbled.

Evaluation of the Catalyst.

Little activity. No stable conversion rates. Probably disintegration of the granules.

SINCLAIR REFINING COMPANY

Oberhausen-Holten
April 13, 1944

S-43

Experiment 688

100 Fe, 5 Cu, 10 CaO, 5 kgr (Soda Precipitation) 3% K_2CO_3 Impregnation

Preparation of the Catalyst PN16 in the laboratory.

45g of kgr are roasted in 50 l of boiling soda solution (6.4 kg of soda, 50 l of water) for one minute. Introducing hot nitrate solution (1.8 kg Fe and the corresponding quantities of Cu and Ca in 50 l of water). Adding 45g kgr. After a short period of stirring, filtration on a suction filter. Sucking off the mother liquor. Washing with 44 l of hot condensate. Treating the catalyst cake which has been sucked dry with 540 cm^3 of potassium carbonate solution (100 g/l) in the kneading machine for 30 minutes. Spreading on trays. Drying in the drier at 120-140° for 24 hours. Forming into 5 mm granules.

Reduction in the 6-ltr-reductor (858)

611 of "Grünkorn" is introduced into the nitrogen-filled apparatus. 35 m^3 of H_2N_2 are passed through at 250-255° for 60 minutes. Cooling down to room temperature in a nitrogen stream. Discharging and saturating under CO_2. Shrinking 25%; reduction value 52% (acetic acid method).

Testing the contact in reactor MR2.

3.85 kg (about 4.5 l) catalyst are filled into the reactor. 10 atü of water gas are pressed on and heated up. Beginning with 150° feed-stock is put through (350-450 l/hr). Already at 203° good conversion rates (61%; Mr = 13). Because of a failure in the heating system, the temperature dropped over a longer period of time, so that the test had to be stopped under pressure. After restarting operation the conversion rate was only 50%. However, the main cause of this decrease is to be seen in a disintegration of the granules, since during the final stage we observed difficulties in the passage of the stock.

Evaluation of the catalyst.

Excellent initial activity. A stop for a longer period of time, mainly however, the disintegration of the granules, caused a reduction of the conversion rate and plugging of the reactor after a short time. On the catalyst having more solidity, it might be possible to attain good results.

SINCLAIR REFINING COMPANY

S-44

April 28, 1947

1697

Oberhausen-Holten
April 13, 1944

Experiment 687

100 Fe, 5 Cu, 10 CaO, 5 kgr (soda precipitation)

Preparation of catalyst PN15 in the laboratory

45 g of kgr are reacted in boiling soda solution (6.4 kg of soda, 50 l of water) for 1 minute. Hot nitrate solution (1.8 kg of Fe and the corresponding quantities of Cu and Ca, 50 l of water) are introduced. Adding 45 g of kgr. After a short period of stirring filtration on the suction filter. Sucking off the mother liquor. Washing with 44 l of hot condensate. Three times treating the catalyst cake with 72 l of hot condensate each time in the settling vat. Filtration on the suction filter. Spreading the catalyst cake on trays. Drying in the dryer.

Reduction in the 6 ltr. reductor (R57).

6 l "Gruenkorn" are introduced into the nitrogen-filled apparatus 35 m^3 H_2N_2 are passed through at 250-256 during 1 hr. Cooling to room temperature with nitrogen. Discharging into CO_2-filled flask and saturating with CO_2.

Testing the catalyst in reactor MR11

3.5 kg (about 5 l) of catalyst are filled into the reactor. Pressing on 10 atü of water gas and heating up. Starting with 150° feed-stock through-put (400 l/hr) and further gradual increase in temperature. Already at 180° heavy methane formation (U=18; Mv=17; X=1.06). At 195° the conversion rate was 32% (Mv=20; X=1.12). At 200° such an excessive methane formation(U=69; Mv=80; X=0.81) occurred that there seemed to be no purpose in continuing the test. Discharging the reactor offered no difficulties.

Evaluation of the catalyst

Catalyst produces nearly exclusively methane. Strong activity.

M. Beth

SINCLAIR REFINING COMPANY

April 28, 1947 1698

Reel 42
Bag 3439-22
Page 405

S-457

Oberhausen-Holten
April 12, 1944

Experiment 686

100 Fe, 5 Cu, 10 CaO, 30 kgr (potassium carbonate formation) 10% KOH impregnation.

Preparation of catalyst PN12 in the laboratory
Same procedure as with PN11 (confer exp. 683), however, stronger alkali-impregnation (1800 cm^3 potassium liquor, 100 g/l).

Reduction in the 6 ltr. reductor (R56)
6 l of "Gruenkorn" are introduced into the nitrogen-filled apparatus. 35 m^3 of H_2N_2 are passed through in one hour. Cooling in the nitrogen stream. Discharging under carbon dioxide and saturating. Shrinking 17%.

Testing the catalyst in reactor MR6
3.15 kg, (about 5 l) are introduced into the reactor. Pressing on 10 atü of water gas and heating up. Beginning with a temperature of 150°, feed stock through-put (350-400 l/hr) and further gradual increase in temperature. After 52 hours of operation at 205° a conversion rate of 52% (Mv=5; X=0.6) is attained. Further increase in temperature does not yield an increased conversion rate. At 215° the conversion rate decreased. Thereupon, the test was discontinued. On opening the reactor the granules were found to have disintegrated, like in the experiments with 5 kgr.

Evaluation of the catalyst
Good activity with slight methane formation. However, the granules disintegrated, whereby the conversion rate was impaired.

M. Beth

SINCLAIR REFINING COMPANY

1699

April 28, 1947

Reel 42
Bag 3439-22
Page 406

5-46

Oberhausen-Holten
March 27, 1944

Experiment 685

100 Fe, 5 Cu, 100 CaO, (soda precipitation) 3% KOH impregnation.

Preparation of catalyst PN14 in the laboratory
Same preparation as PN8 (conf. exp. 677, page 412).

Reduction in the 6 ltr. reductor (R55)
6 l. of "Gruenkorn" are introduced into the nitrogen-filled apparatus. 35 m^3 of H_2N_2 are put through at 252-254° during one hour. Cooling in the hydrogen stream to room temperature. Discharging under CO_2 and saturating with CO_2. Shrinking 15%.

Testing the contact in the reactor MR10
3.9 kg (about 5 l) of Gruenkorn ~~(sic!)~~ are filled into the reactor. Pressing on10 atü of water gas and heating up. Starting with 150° feed-stock through-put (350-400 ltr/hr) and further gradual temperature increase. Initially slight methane formation. At 206° a conversion rate of 41% (Mv=3) was attained. In spite of raising the temperature to 214°, the conversion rate did not increase any more substantially (U=49; Mv=9; X=0.53). Soon thereafter, in spite of a further raise in temperature, the conversion rate dropped sharply. The passage of the stock deteriorated constantly. When the apparatus was completely plugged up, the experiment was terminated. On opening the reactor, the granules were found to have disintegrated and to have formed a viscous mass with the paraffin which had been imperfectly discharged because of this situation. The contact-paraffin mixture had furthermore run through the screen and had congealed in the unheated bottom section of the reactor. Discharging the reactor was very difficult.

Evaluation of the catalyst.
Forms little methane; granules disintegrate. (Confer. exp. 684, page 407).

M. Beth

SINCLAIR REFINING COMPANY

1700

April 28, 1947

Reel 42
Bag 3439-22
Page 407

S-47

Oberhausen-Holten
March 27, 1944

Experiment 684

100 Fe, 5 Cu, 10 CaO, 5 kgr (potash precipitation)x 3% KOH-impregnation

Preparation of catalyst PN10 in the laboratory

50 g of kieselgur are reacted in a boiling potasch solution (8.3 kg of potash, 50 l of water) for one minute. Introducing a hot nitrate solution (50 l with 1.8 kg Fe and the corresponding Cu and Ca quantities). Adding 50 g kgr. After a short period of stirring filtering on the suction filter (1.3 m^2). Sucking off the mother liquor. Washing with 72 l of hot condensate. Treating the catalyst cake which had been sucked dry with 540 cm^3 of caustic potash solution (100 g KOH/l) in the kneading machine for 30 minutes. Spreading of the cake on trays. Drying in the drier at 120°-140° for 24 hours. Pressing through a 4 mm screen.

Reduction in the 6 l reductor (R54)

6 l of "Gruenkorn" are filled into the nitrogen filled apparatus. 35 m^3 of HN_2 (sic!) are passed through at 254-257° during one hour. Cooling to room temperature in an oxygen free nitrogen stream. Discharging and saturating with carbon dioxide. A raise in temperature occurred thereby. Shrinking :17%.

Testing of the catalyst in reactor MR5

4.15 kg (about 6 l) of catalyst are introduced into the reactor. 10 atü of water gas is pressed on and heated up. Starting with 150°, feed stock is put through (400-450 l/hr) and the temperature is gradually raised. Initially methane formation was Mv = 6. Only at 212° a conversion rate of 55% was attained (Mv = 8), which failed to rise in spite of the temperature's being raised to 220°; on the contrary, it dropped. Since it was found out later on that the catalyst and paraffin had penetrated through the upper screen into the lower unheated section of the reaction, the decrease in the conversion rate may be caused thereby. A thorough examination that all over the reactor the granules had disintegrated. By getting mixed with the paraffin formed a paste-like mass was formed, which pressed itself

x Analysis of the "Gruenkorn" in the laboratory showed:
100 Fe, 4.7 Cu, 5.58 CaO, 4.6 kgr.
Alkalinity: 204 cm^3 n HCl consumption/100 g catalyst.

through the sieve. We may, therefore, trace back the drop in the conversion rate to the disintegration of the catalyst, whereby the paraffin failed to be carried out. Discharging the reactor proved to be most difficult, since the paraffin could not be carried out by means of hot hydrogen.

Evaluation of the catalyst

Slight activity (212°: U = 55); comparatively low methane formation (Mv = 8); working-up ration poor (X = 0.58). Because of its disintegration an unobjectionable test was only possible up to 212°.

M. Beth

Oberhausen-Holten
March 25, 1944

Experiment 682

100 Fe, 5 Cu, 10 CaO, 5 kgr (caustic potash solution precipitation) x)
3% KOH impregnation

Preparation of catalyst PN9 in the laboratory
50 g kgr is reacted in boiling caustic potash solution (6.8 kg potassium hydroxide, 50 l of water) for one minute. Introducing hot nitrate solution (50 l with 1.8 kg Fe and the corresponding quantities of Cu and Ca). Adjusting to pH= 9.3 by adding 7 l of caustic potash solution (135 KOH/l), putting in 50 g kgr. After a short period of stirring filtration on the suction filter (1.3 m^2). Sucking off of the mother liquor. Washing with 44 l of hot condensate. Treating the catalyst cake which has been sucked dry, with 540 cm^3 of caustic potassium solution (100 g of KOH/l) in the kneading machine for 30 minutes. Spreading the cake on trays. Drying in the drier at 120° -140° for 24 hours. Pressing through a 4 mm screen.

Pretreatment of the "Grunkorn" (unreacted catalyst)
The "Grunkorn" is heated up in the igniting furnace with air at 430° for 24 hours.

Reduction in the 6 ltr reductor (R53)
6 l of pretreated "Gruenkorn" is introduced into the nitrogen filled apparatus. 35 m^3 of H_2N_2 are passed through at 250° during one one hour. Cooling down in an oxygen-free nitrogen stream to room temperature. Discharging and saturating with carbon dioxide. Thereby occurred an increase in temperature.

Testing of the catalyst in reactor MR2
4.19 kg (about 5 l) of catalyst are charged into the reactor. 10 atü water gas are pressed on and heated up. Starting wi 150°, gas is put through (400 l/hr.) and the temperature is gradually raised. At 190° a conversion rate of 44% (M=51) was measured. In spite of great precaution in raising the temperature, at 197° much methane formation occurred again (Mv = 40). Thereupon the conversion rate dropped to about 20 and the methane formation decreased. Without raising the temperature, at 210 the methane formation rose from Mv = 4 (sic!) to Mv = 87. Thereupon, the test was terminated, since after the methane formation's gradual dropping, the conversion rate dropped considerably.

Evaluation of the catalyst

Already at 190° considerable methane formation. Likewise at higher temperatures

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X) The Gruenkern analysis gave:
100 Fe, 4.83 Cu, 7.86 CaO, 4.4 kgr.
Alkalinity 18 cm^3 $\frac{n}{10}$ HCl consumption/100 g of catalyst.

M. Beth

SINCLAIR REFINING COMPANY

1704

April 29, 1947

S-49

Reel 42
Bag 3439-22
Page 409

Oberhausen-Holten
April 13, 1944

Experiment 680

100 Fe, 5 Cu, 10 CaO, 30 kgr[x] (caustic soda solution precipitation)
3% KOH impregnation

Preparation of catalyst PN7 in the laboratory

55 g of kgr are reacted in a boiling caustic soda solution (4.0 kg sodium hydroxide, 47 l of water) for one minute. Pouring in hot nitrate (50 l with 1.8 kg Fe and the corresponding quantities of Cu and Ca). 485 g of kgr are put in, after adjusting to pH = 9.3 by adding 2 l of caustic soda solution (85 g of KOH/l). After a short period of stirring, filtering on the suction filter. Sucking off of the mother liquor. Washing with 44 l of hot condensate. Treating the catalyst cake after its being sucked dry with 540 cm^3 of caustic potash solution (100 g of KOH/l) in the kneading machine during 30 minutes. Spreading of the cake on trays. Drying in the drier at 120-140° during 24 hrs. Pressing through a 4 mm screen.

Reduction in the 6 ltr reductor (R62)

6 l of "Grunkorn" are introduced into the nitrogen filled apparatus. 35 m^3 of H_2N_2 are passed through at 318-327° for 75 minutes. Cooling down to room temperature in an oxygen-free nitrogen stream. Discharging and saturating with carbon dioxide. Thereby calefaction up to 70° occurred.

Testing the catalyst in reactor MR1

2.67 kg (about 5 l) of catalyst are introduced into the reactor. 10 atü of water gas are pressed on and heated up. Starting with 150° feed stock is put through (400-450 l/hr.) and the temperature is gradually raised. Starting with 200° the methane formation was Mv = 15. After 102 hours of operation a conversion rate of 60% (Mv = 20) was attained. By gradually increasing the temperature up to 220° up to 380th hour of operation the conversion rate could be maintained at 60%. Then, heavy methane formation occurred for a short period of time (Mv = 45). Thereby, the conversion rate dropped at first to 50% and after 700 hours of operation to 40%. The methane formation remained at 15%. The test was terminated after 962 hours of operation.

Evaluation of the catalyst

Good activity (Mv=20); operating temperature 222°; pure white paraffin

M. Beth

x) The "Grunkorn" analysis showed: 100 Fe, 5.72 Cu, 5.68 CaO, 21.5 kgr. Alkalinity 108 cm^3 HCl consumption/100 g. catalyst.

SINCLAIR REFINING COMPANY

1105

April 29, 1947

S-50

Reel 42
Bag 3439-2
Page 410

Oberhausen-Holten
April 5, 1944

Experiment 679

100 Fe, 5 Cu, 10 CaO, 30 kgr (caustic potash solution precipitation)x)
3% KOH impregnation

Preparation of catalyst PN6 in the laboratory

55 g of kgr are reacted in a boiling caustic potash solution (7.1 kg of potassium hydroxide, 52.5 l of water), for one minute. Hot nitrate solution (50 l with 1.8 kg of Fe and the corresponding quantities of Cu and Ca) is introduced. Adjusting to pH = 9.3 by adding 4.5 l caustic potash solution (130 g of KOH/l); 485 g of kgr are put in. After a short period of stirring filtering on the suction filter (1.3 m^2). Sucking off the mother liquor. Washing with 44 l of hot condensate. Treating the catalyst cake, after its being sucked dry, with 540 am^3 of caustic potash solution (100 g. of KOH/l) in the kneading machine for 30 minutes. Spreading of the catalyst cake on trays. Drying in a drier at 120-140° for 24 hours. Pressing through a 4mm screen.

Reduction in the 6 ltr. reductor(R51)

6 l of catalyst are introduced into the nitrogen filled apparatus. 38 n of H_2N_2 are passed through at 320-325° during one hour. Cooling off in an oxygen-free nitrogen stream to room temperature. Discharging under CO_2 protection and saturating with carbon dioxide. Thereby, calefaction occurred.

Testing the catalyst in the reactor MR8

2.69 kg (about 5 l) of catalyst are filled into the reactor. Pressing on 10 atü of water gas and heating up. Starting with 150°, feed stock is put through (400-450 l/hr) and the temperature is gradually raised. Up to 195° methane formation was slight (Mv = 4). Starting with 200° it averaged Mv = 15. At 217° after 117 hours of operation a conversion rate of 64% was attained (Mv = 15; X = 0.7). By gradually raising the temperature to 221°, over a longer period of operation (450 hours) a conversion rate of 60% could be maintained. During this period the methane formation averaged Mv = 16. Then, heavy methane formation started all of a sudden (Mv = 57). After the methane formation's settling down, in spite of raising the temperature, the maximum conversion rate attained was 47% (Mv = 10). The test was terminated after 810 hours of operation. Carbon had been deposited in the upper layers. Unfavorable operating conditions are probably responsible for the sudden methane formation (insufficient water filling of the reactor).

Evaluation of the catalyst

Good activity averaging Mv = 16; operating temperature 221°; working-up ratio X = 0.7. After 670 hours of operation conversion rate 61% at 221°. Pure white paraffin.

M. Beth -

x) The "Grunkorn"analysis showed: 100 Fe, 5.17 Cu, 4.28 CaO, 19.5 kgr. Alkalinity 102 cm^3 n HCl consumption/100 g. catalyst.

SINCLAIR REFINING COMPANY

1707

April 29, 1947

Reel 42
Bag 3439-22
Page 411

S - 5-1

Oberhausen-Holten
March 24, 1944

Experiment 678

100 Fe, 5 Cu, 10 CaO, 30 kgr (potash precipitation)x) 3% KOH impregnation.

Preparation of the catalyst PN5 in the laboratory

55 g. of kieselgur are reacted in a boiling potash solution (8.3 kg of potash, 50.4 l of water) for one minute. Hot nitrate solution (50 l with 1.8 kg of Fe and the corresponding quantities of Cu and Ca) is introduced. Putting in 485 g. of kgr. After stirring for a short time, filtering in the suction filter (1.3 m^2). Sucking off of the mother liquor. Washing with 44 l of hot condensate. Treating the catalyst cake which has been sucked dry with 540 cm^3 of caustic potassium solution (100 g of KOH/l) in the kneading machine for 30 minutes. Spreading of the cake on trays. Drying in the drier at 120-140° (24 hrs.). Pressing through a 4 mm screen.

Reduction in the 6 ltr. reductor (R50)

6 l of "Grunkorn" are introduced into the nitrogen filled apparatus. 35 m^3 of H_2N_2 are passed through at 315-327° during one hour. Cooling in the N_2 stream to normal temperature. Discharging under N_2 and saturating with CO_2. Thereby, calefaction to about 60-70° occurred. Shrinking 15%.

Testing the catalyst in reactor MR7

2.8 kg (about 5 l) of catalyst are introduced into the reactor. Pressing on of 10 atü water gas and heating up. Starting with 150°, feed stock was put through (400-500 l/hr.) and the temperature was gradually increased furthermore. Initially, up to 195° hardly any methane was formed (Mv = 2); after 84 hours of operation at 204° a conversion rate of 55% (Mv = 7) was attained. In spite of raising the temperature still more to 222° the optimum conversion rate averaged 53%. The methane values averaged Mv = 11. The working-up ratio averaged X = 0.62. After 348 hours of operation the test was terminated.

Evaluation of the catalyst

Slight activity. Comparatively low methane formation. Poor working-up ratio (222°: U = 53; Mv = 11; X = 0.62).

M. Beth

x) The "Gruenkorn" analysis gave: 100 Fe, 4.9 Cu, 10.0 CaO, 24.1 kgr. Alkalinity 244 cm^3n HCl/100 g catalyst.

SINCLAIR REFINING COMPANY

April 29, 1947 1708

Reel 42
Bag 3439-22
Page 412

5-52

Oberhausen-Holten
February 2, 1944

Experiment 677

100 Fe, 5 Cu, 10 CaO, 5 kgr (soda precipitation)x) 3% KOH impregnation

Preparation of the catalyst PN8 in the laboratory
45 g of kieselgur are reacted in a boiling soda solution (6.4 kg of soda, 50.4 l of water) for one minute. Hot nitrate solution (50 l with 1.8 kg of water and the corresponding quantities of Cu and Ca). 45 g. of kieselgur are put in. After a short period of stirring filtration on the suction filter (1.3 m^2). Sucking off of the monthe liquor. Washing with 44 l of hot condensate. Sucking the catalyst cake dry and treating it with 540 cm^3 of caustic potash solution (100 g. of KOH/l) in the kneading machine for 30 minutes. Spreading the cake on trays. Drying in the drier at 120°. Pressing through a 4 mm screen.

Reduction in the 6 ltr. reductor (R49)
Preparation in two charges (4 l and 3 l). Filling the Grunkorn into the N_2 filled apparatus. Passing through H_2N_2 at 250-256° during one hour (6 m^3/1/1 of catalyst). Cooling down to room temperature with O_2 free nitrogen. Discharging in CO_2 atmosphere and saturating with CO_2. Thereby, calefaction occurred up to 60-70° Shrinking about 25%.

Testing the catalyst in reactor MR4
3.89 kg of catalyst are introduced into the reactor. 10 atü of water gas are pressed and heated up. Starting with 150°, feed stock is put through (400 l/hr.) and the temperature is gradually raised some more. At 208° a conversion rate of 50% was attained, the methane values being very low (Mv = 6). But, all of a sudden, the conversion rate dropped and could not be restored to its previous height, not even by raising the temperature. When the reactor did not let any stock pass any more, the experiment was terminated. On opening the reactor the carbon deposit was to be found in the upper screen had been crushed, so that a part of the catalyst could not get into that section of the reaction chamber which was surrounded by the heating jacket. Apparently, because of insufficient heat removal, excessive heat had developed at that place, which caused the carbon deposit. Discharging the lower part of the reactor was difficult.

Evaluation of the catalyst

Slight methane formation. Because of a failure of the apparatus, it could be tested only up to 208°. Up to this temperature, satisfactory conversion rates and low methane formation (U = 54; Mv = 7; X = 0.50).

K. Beth

X) The "Gruenkorn" analysis showed: 100 Fe, 5.02 Cu, 3.06 CaO, 4.2 kgr. Alkalinity 136 cm^3 n HCl consumption/100 g of catalyst.

SINCLAIR REFINING COMPANY

1710

April 29, 1947

Reel 42
Bag 3439-22
Page 413

S-53

Oberhausen-Holten
February 23, 1944

Experiment 676

100 Fe, 5 Cu, 10 CaO, 30 kgr (soda precipitation)x) 3% KOH impregnation

Preparation of catalyst PN4 in the laboratory

50 g. of kieselgur are reacted in boiling soda solution. (6.4 kg of soda, 4 l of water) for one minute. Hot nitrate solution (50 l with 1.8 Fe and the corresponding quantities of Cu and Ca are introduced. 485 g. of kgr are put in. After a short period of stirring filtering on the suction filter (1.3 m^2). Sucking off the mother liquor. Washing with 44 l of hot condensate. Sucking dry the contact cake and treating it with 540 cm^3 of caustic potassium solution (100 g. of KOH/l) on the kneading machine for 20 minutes. Spreading the cake on trays. Drying in the drier at 120°. Pressing through a 4 mm screen.

Reduction in the 6 ltr. reductor (R49)

6.2 l of "Grunkorn" is introduced into the N_2 filled apparatus 35 m^3 of H_2N_2 are passed through at 317-323° for one hour. Cooling down to 60° with O_2 - free nitrogen. Soaking with CO_2 until room temperature is reached.

Testing the catalyst in reactor MR6

2.91 kg (5 l) are filled into the reactor. 10 atü water gas are pressed on and heated up. Starting with 150°, feed stock is put through (400-450 l/hr). Up to 205° only slight methane formation at a conversion rate of 38% (Mv = 6). At 205° suddenly heavy methane formation took place, which, however, dropped to Mv = 8 later on. At the same time the conversion rate decreased currently. A raise in temperature to 222°did not cause any increase in the conversion rate. The catalyst was distinctly inactive (222°: U = 34; Mv = 8). The convertor discharge was difficult because of the carbon deposits occurring in the upper section of the reactor.

Evaluation of the catalyst

Tendency towards forming methane (205°: Mv - 51). After the methanization, a poor conversior rate, in spite of using higher temperatures (222°: U = 34; Mv = 8).

M. Beth

x) The "Gruenkorn" analysis gave: 100 Fe, 6.02 Cu, 8.08 CaO, 228 kieselgur. Alkalinity 274 cm^3 consumption n/10 HCl/100 g catalyst.

SINCLAIR REFINING COMPANY

1711

April 29, 1947

3-54

Reel 42
Bag 3439-22
Page 414

Oberhausen-Holten
April 5, 1944

Experiment 675

100 Fe, 5 Cu, 10 CaO, 10 kgr (potash precipitation) 3% KOH impregnation

Preparation of catalyst PN3 in the laboratery
53 g of kieselgur are reacted in a boiling potash solution (8.5 kg of potash) for one minute. A hot nitrate solution is introduced (49 l with 1.75 kg Fe and the corresponding quantities of Cu and Ca). Putting in 465 g. of kieselfur. After a short period of stirring filtration on the suction filter (1.3 m^2). Sucking off the mother liquor. Washing with 84 l of hot condensate. Treating the catalyst cake, after sucking it dry, with 525 cm^3 of caustic potash solution (100 KOH/l) in the kneading machine for 30 minutes. Spreading the cake on trays. Drying in the drier at 140°. Pressing through a 4 mm screen.

Reduction in the 6 ltr. reductor (R47)
6.2 l of "Gruenkorn" are introduced into the nitrogen filled apparatus. 35 m^3 of H_2N_2 are passed through at 325° during one hour. Cooling down with oxygen-free nitrogen (1 hr.). Discharging under N_2. Shrinking 19%.

Testing the catalyst in the reactor MR3
Introducing 2.55 kg of catalyst into the reactor. Pressing on 10 atü of water gas and heating up. Starting with 150° feed stock through-put (350-400 l/hr) and further increase in temperature. After 91 hours of operation at 219° a conversion rate of 82% was found (Mv = 21). The methane formation did not vary much during the initial period (Mv = 15). The temperature was increased to 221.5°. The conversion rate was gradually dropping from 67% to about 50%. After the temperature had been raised to 222.5°, the conversion rate averaged 55% from the 314th to the 700th hour. The methane values varied between Mv = 15 to Mv = 20. After 700 hours of operation the feed stock was recycled. The conversion rate failed to be improved thereby, the methane values dropped somewhat, and the working ratio rose to 0.8. The experiment was terminated since no new results could be expected.

Evaluation of the catalyst
Medium activity (U = 55). High methane formation (Mv = 15-20)
Time of operation 700 hrs. Brown paraffin. Operating temperature 222°.

M. Beth

x) The "Gruenkorn" analysis gave: 100 Fe, 6.1 Cu, 8.9 CaO, 26.7 kgr. Alkalinity 150 cm^3 $\frac{n}{10}$ HCl consumption/100 g catalyst.

SINCLAIR REFINING COMPANY

1712

April 29, 1947

Reel 42
Bag 3439-22
Page 415

S-55

Oberhausen-Holten
February 9, 1944

Experiment 671

100 Fe, 5 Cu, 10 CaO, 30 kieselgur/caustic soda solution precipitation)
3% KOH impregnation

Preparation of catalyst PN2 in the laboratory

53 g. of kgr are reacted in 42 l of boiling caustic soda solution (3.57 kg NaOH) for one minute. Introducing hot nitrate solution (49 l with 1.75 kg Fe and the corresponding quantities of Cu and Ca). Adjusting to pH = 9.3 by adding 7 l of caustic soda solution (85 g NaOH/l). Pouring in 462 g of kieselgur. Stirring for a short period of time, then filtering on the suction filter (1.3 m^2). Sucking off the mother liquor. Washing with 42 l of hot condensate (4 times with 10 l each). Treating the catalyst cake which had been sucked dry with 525 cm^3 of caustic potash solution (100 g of KOH/l) in the kneading machine for 30 minutes. Spreading the cake on trays. Drying in the drier at 140°. Pressing through a 4 mm screen.

Reduction in the 6 ltr. reductor (R45)

Introducing 6.2 l of "Grunkorn" into the nitrogen filled apparatus. Passing through 35 m^3 of H_2N_2 (75% of H_2) at 325° during one hour.

Testing the catalyst in reactor MR1

2.68 kg (5 l) of catalyst are introduced into the reactor. 10 atü of water gas are pressed on and heated up. Starting with 150° feed stock is put through (400 to 450 l/hr) and the temperature is furthermore raised. The conversion rate increased rather uniformly from about 20% at 180° to 61% at 220° within 150 hours of operation. During this period of time the methane formation averaged Mv = 18. After the experiment's having run for some time at 220°, suddenly a very heavy methane formation occurred (Mv = 53 at a conversion rate of 63-70%). Soon thereafter difficulties in the feed-stock throughput were observed. Thereupon, the test was discontinued. On opening the reactor elementary carbon was found in the upper section. Discharging difficulties were met with only in the uppermost layer.

Evaluation of the catalyst

The catalyst operates at a comparatively high temperature (220° U = 61; Mv = 18; X = 0.66) and tends towards spontaneous methane formation (220°: Mv = 53).

M. Beth

SINCLAIR REFINING COMPANY

1713

April 30, 1947

S-56

Reel 42
Bag 3439-22
Page 416

Oberhausen-Holten
February 22, 1944

Experiment 670

100 Fe, 5 Cu, 10 CaO, 50 kgr (caustic soda solution precipitation)
3% KOH impregnation

Preparation of catalyst F2219 in the laboratory

Preparation of individual charges containing 25 g of Fe each. Reacting of 2 g of kgr in 630 cm^3 of caustic soda solution (538 g. NaOH/l) by boiling it for one minute. Introducing a boiling nitrate solution, namely 175 cm^3 of Fe - nitrate solution (143 g. Fe/l); 7.1 cm^3 Cu-nitrate solution (176 g. Cu/l); 12.1 cm^3 Ca - nitrate solution (107 g. CaO/l). Adjusting to p_H = 9.3. Adding 11 g. of kieselgur. Filtration on suction filter. Washing with 600 cm^3 of hot condensate. Impregnating the catalyst cake on a tray with 7.5 cm^3 of potash solution (100 g KOH/l). Spreading the cake on trays. Drying in the drier at 106° (24 hrs). Forming 1.5 mm granules.

Reduction in the 6 ltr. reductor (R46)

6.2 l of "Gruenkorn" are introduced into the nitrogen filled apparatus. 35 m^3 of H_2N_2 (75% H_2) are passed through at 325° during one hour. Cooling down with oxygen free nitrogen during one hour. Discharging under N_2. Shrinking 14%.

Testing the catalyst in reactor MR5

2.2 kg (about 5 l) of catalyst are introduced into the reactor. 10 atü water gas are pressed on and heated up. Starting with 180°, feed stock is put through (400 l/hr) and the temperature is further increased. The conversion rate rose slowly, the methane formation remaining unchanged (Mv = 17). On attaining a temperature of 223°, a conversion rate of 64% was observed (Mv = 18). The conversion rate remained constant at this temperature for 150 hours of operation. Thereafter, it began decreasing. For this reason, the test was terminated (343 hours of operation). On opening the reactor no carbon deposit was found.

Evaluation of the contact

Already starting at 190° rather heavy, but constant methane formation (Mv = 18). At 223° a fair conversion rate (U = 64%); working-up ratio X = 0.7. After some period of operation drop in the conversion rate.

Up till this date, the best catalyst is the 50 g of kieselgur series.

M. Beth

SINCLAIR REFINING COMPANY

1114

April 30, 1947

S-57

Reel 42
Bag 3439-22
Page 417

Oberhausen-Holten
February 9, 1944

Experiment 669

100 Fe, 5 Cu, 10 CaO, 50 kgr (caustic soda solution precipitation)
3% KOH impregnation

Preparing catalyst PN1 in the laboratory

75 g. of kieselgur are reacted in 30 l. of boiling caustic soda solution (about 85 g. of NaOH/l) for one minute. Hot nitrate solution is added (11.6 l of Fe-nitrate solution (107.5 g Fe/l) 1.25 kg Fe + 0.69 l Cu-nitrate solution (90.5 g Cu/l) + 1.04 l Ca-nitrate solution (120 g CaO/l) + 21.6 of water). Adjusting to p_H = 9.3 by adding 2.5 l of caustic soda solution. Filtration on suction filter (1.3 m^2). Sucking off the mother liquor. Washing with 30 l of hot condensate. Treated the catalyst cake which has been sucked dry with 375 cm^3 of caustic potash solution (100 g. KOH/l) in the kneading machine for 30 minutes. Spreading the cake on trays. Drying in the drier at 140°. Pressing through a 4 mm^2 screen to form 3 mm granules.

Reduction in the 6 ltr. reductor (R43)

6.2 l of "Gruenkorn" are introduced into a nitrogen filled apparatus. 35 m^3/hr of H_2N_2 are passed through at 380° for 24 hours. Cooling down with O_2 free nitrogen. Discharging under nitrogen. Shrinkage 20%. Reduction value 79%.

Testing the catalyst in the reactor MR4

2.15 kg (about 5 l) of catalyst are introduced into the reactor. 10 atü of water gas are pressed on and heated up. Starting with 150°, feed stock is put through (350-400 l/hr) and the temperature is gradually increased furthermore. In the 190-200° temperature range rather heavy methane formation (Mv = 16) at an average conversion rate of 25% and a favorable consumption ratio (X = 1.0). Between 204 and 207° increasing methane formation (Mv = 30) with a constant conversion rate and a decreasing consumption ration (X = 0.85). Between 208 and 213° the conversion rate rises to U = 35 (Mv = 20-sic!). By raising the temperature to 220°, the conversion rate could be raised only slightly (U = 46) while the methane formation rose steeply (Mv = 50). After the methane formation had decreased, in spite of raising the temperature to 223° only a maximum conversion rate of 37% could be attained with the methane formation continued to be heavy (Mv = 22°). On opening the reactor, a slight carbon deposit was found in the uppermost layer. Discharging the reactor met with no difficulties.

Evaluating the contact

Already at low temperatures (190-205°) a strong inclination towards forming methane. At 220° a mediocre conversion rate with strong methane formation (U = 46; Mv = 50). Thereafter, in spite of applying higher temperatures, low conversion rates with continuing high methane values (U = 37; Mv = 22; X = 0.74). The catalyst shows a distinct tendency towards forming methane.

H. Beth

SINCLAIR REFINING COMPANY

1716

April 30, 1947

Reel 42
Bag 3439-22
Page 418

S-58

Experiment 668

100 Fe, 5 Cu, 10 CaO, 25 kgr (caustic potassium solution precipitation)
3% KOH impregnation

Preparation of catalyst F2220 in the laboratory

0.3 kg of kieselgur are reacted in a boiling caustic potassium solution 19 kg of potassium hydroxide, 190 l of water) for one minute. Hot nitrate solution is introduced (36 kg of Fe-nitrate, 1.5 kg of Cu-nitrate, 1.0 kg of Cu-nitrate, 120 l of water). 1.8 kg of kieselgur are added. Stirring for one minute. Filtering through filter press. Washing with hot condensate (30 min.). Drying with air (10 min.). Treating the catalyst cake, with potassium hydroxide (0.18 kg, 8 l of water) in the Esch-mixer for 30 minutes. Spreading the cake on trays. Drying in the drier at 140°. Granulation to 1-3 mm.

Reduction in the 6 ltr. reductor (R42)

2 charges (3.5 l and 4.0 l). Introducing the "Gruenkern" into the nitrogen filled apparatus. Passing through H_2N_2 (75% H_2) at 325° for one hour. Cooling down with O_2 free nitrogen. Discharging under N2. Shrinking 28%.

Testing the catalyst in reactor MR2

3.22 kg (about 4.9 l) of catalyst are introduced into the reactor. 10 atü water gas are pressed on and heated up. Starting with 150° feed stock is put through (400-450/hr.) and the temperature is raised still more. At 200° a conversion rate of 40% (Mv = 11) was attained. On raising the temperature still more, little methane formed during the reaction. A satisfactory conversion rate was obtained only at 225° (U = 58; Mv = 10; X = 0.72). It is possible that this high temperature was necessitated by a rather prolonged discontinuation of the operation, caused by a drop in temperature. After 300 hours of operation, the conversion rate was 56%, the methane formation Mv = 7, the working-up ratio X = 0.77. Discharging the reactor met with no difficulties.

Evaluation of the catalyst

The catalyst operates with a comparatively low methane formation (average methane Mv = 8). Operating temperature rather high (222-225°); this, however, may be caused by a stopping in the operation. Maximum conversion 58%. Consumption ratio X = 0.77.

M. Beth

SINCLAIR REFINING COMPANY

1717

April 30, 1947

S-59

Reel 42
Bag 3439-22
Page 420

Oberhausen-Holten
February 3, 1944

Experiment 665

100 Fe, 10 Cu, 10 CaO, 50 kgr (caustic soda solution precipitation)
10% KOH impregnation

Preparation of catalyst F2218 in the laboratory

0.6 kg of kieselgur is reacted with boiling caustic soda solution (12.2 kg of NaOH, 190 l of condensate) for one minute. Hot nitrate solution (36 kg of Fe-nitrate, 1.5 kg of Ca nitrate, 2.0 kg of Cu-nitrate, 120 l of water) are added. Putting in 2.4 kg of kieselgur. After a short period of stirring, filtering through filter press. Washing with hot condensate (30 min.). Drying with air (10 min.). Treating the catalyst cake in the Esch mixer with an addition of potassium hydroxide (600 g. KOH, 2 l of water for 30 minutes. Predrying of the cake in the drier at 80° for 3 hours. Spreading on trays and drying at 140° in the drier. Forming 1-3 mm granules.

Reduction in the 6 ltr. reductor (R39)

6.2 l of "Gruenkorn" are introduced into the nitrogen filled apparatus. 35 m^3/hr of H_2N_2 (75% H) are passed through at 380° for 24 hrs. Cooling down in one hour with O2-free nitrogen. Discharging under nitrogen.

Testing the catalyst in reactor MR1

2.64 kg (about 5 l) of catalyst are introduced into the reactor. Pressing on 10 atü of water gas and heating up. Starting with 1500 feed stock (450-500 l/hr) is put through while raising the temperature gradually to 200°. At this temperature the conversion rate was 36% (Mv = 8; X = 0.51). In order to attain higher conversion rates, the temperature had to be raised to 223° within 60 hours. For about 70 hours the conversion rate averaged 60% (Mv = 12; X = 0.67); thereafter, it began dropping. For this reason, the experiment was terminated. The reactor was easy to discharge.

Evaluation of the catalyst

Slight activity. Only at a temperature of more than 220° satisfactory conversion rates (U = 60%; Mv = 12, X = 0.67), which, however, dropped after a short period of time.

M. Beth

SINCLAIR REFINING COMPANY

1718

April 30, 1947

5-60

Reel 42
Bag 3459-22
Page 419

Oberhausen-Holten
February 1, 1944

Experiment 667

100 Fe, 10 Cu, 10 CaO, 50 kgr (caustic soda solution precipitation)
10% KOH impregnation

Preparation of catalyst F2218 in the laboratory
Confer experiment 665

Pretreatment of the "Gruenkorn"
The "Gruenkorn" is heated up with air in the ignitor for 24 hrs. Shrinking 14%.

Reduction in the 6 ltr. reductor (R41)
6 l of pretreated "Gruenkorn" are introduced into the nitrogen filled apparatus. 35 m^3 of H_2N_2 (75% H_2) are passed through at 325° during one hour. Shrinkage 12%.

Testing the catalyst in reactor MR3
2.71 kg (about 4.6 l) of catalyst are introduced into the reactor. 10 atü of water gas are pressed on and heated up. Starting with 150°, feed stock (450-500 l/hr) is put through, increasing the temperature still further to 206°. At this temperature a conversion rate of 64% was attained (Mv = 36), which however, dropped to U = 47 after a short period of time (Mv = 19). In spite of a further increase in temperature to 221° in the course of 80 additional hours of operation the maximum conversion rate attained was only 56% (Mv averaging 16). For this reason, the experiment was discontinued.

Evaluation of the catalyst
In the 200-205° range good initial activity, but high methane formation and quickly dropping conversion rates. In spite of an increase in temperature to 221° unsatisfactory conversion rates at comparatively high methane formation (U = 55; Mv = 15; X = 0.67).

M. Both

SINCLAIR REFINING COMPANY

1719

May 1, 1947

S-61

Reel 42
Bag 3439-22
Page 421

Oberhausen-Holten
January 28, 1944

Experiment 664

100 Fe, 10 Cu, 10 CaO, 50 kgr (caustic soda solution precipitation)
10% KOH impregnation

Preparation of catalyst F2217 in the laboratory

0.5 kg of kieselgur are treated with boiling caustic soda solution (12 kg of NaOH, 190 l of condensate) for one minute. Introducing a hot nitrate solution (36 kg of Fe - nitrate, 1.5 kg of Ca - nitrate, 2.0 kg of Cu - nitrate, 120 l of water). Adding 2.4 kg of kgr. For the purpose of effectuating the complete precipitation of the nitrates, 0.7 kg of NaOH are added. After a short period of stirring, filtration through the filter press. Washing with hot condensate (30 minutes). Drying with air (10 minutes). Treating the catalyst cake with an addition of potassium hydroxide (600 g. KOH, 2 l of water) in the Esch mixer for 30 minutes. Predrying of the cake in the drier at 80° for 3 hrs. Spreading on trays and drying at 140° in the drier. Forming 1-3 mm granules.

Reduction in the 6 ltr. reductor (R38)

6.2 l of "Grunkorn" are introduced into the nitrogen filled apparatus. 35 m^3 of H_2N_2 (75% of H_2) are passed through at 320° during one hour. Cooling with O_2-free nitrogen during one hour. Discharging under N_2. Shrinking 13%.

Testing the catalyst in the reactor MR3

2.97 kg (about 5 l) of catalyst are introduced into the reactor. 10 atü of water-gas are pressed on and heated up. Starting with 150°, feed stock (450-511 l/hr) are put through, while raising the temperature to 218°. At this temperature, the conversion rate was U = 47, the methane formation Mv = 7, the working-up ratio X = 0.5. On raising the temperature still more to 222°, the conversion rate did not improve. For this reason, the test was discontinued. The reactor was easy to discharge.

Evaluation of the catalyst

Slight activity. Only in the 220° temperature range mediocre conversion rates (U = 47; Mv = 7). Poor working-up ratio X = 0.5.

Since a considerable alkali hydroxide excess was employed at the precipitation, the catalyst does not quite correspond to the quality desired.

M. Beth

SINCLAIR REFINING COMPANY

1720

May 1, 1947

S-62

Reel 42
Bag 3439-22
Page 423

Oberhausen-Holten
January 28, 1944

Experiment 662

100 Fe, 5 Cu, 10 CaO, 50 kgr (caustic potash solution precipitation)
3% KOH - impregnation

Preparation of catalyst F2216 in laboratory

Preparation in individual charges of 25 g of Fe each. 2 g of kgr are treated in 730 cm^3 of boiling caustic potash solution (98.5 g. KOH) for 15 seconds. 700 cm^3 of boiling nitrate solution (25 g. of Fe, 1.25 g. of Cu, 2.5 g. of CaO) are added. Adjusting to pH = 9.3. Adding 11 g of kieselgur. Filtration on suction filter. Washing with 600 cm^3 of hot condensate. Impregnating the catalyst cake on a tray with 7.5 cm^3 of caustic potash solution (100 g KOH/l). Spreading the cake on trays. Drying in the drier at 106° (24 hrs.). Forming 1.5 mm granules.

Reduction in the 6 ltr. reductor (R36)

6 l of "Gruenkorn" is introduced into the nitrogen-filled apparatus. 35 m^3/hr of H_2N_2 (75% H_2) are put through at 370° for 24 hours. Cooling down with O_2-free nitrogen during one hour. Discharging under N_2. Shrinking 21.5%; reduction value 91%.

Testing the catalyst in reactor MR1

1.935 kg (about 4.5 l) are introduced into the reactor. 10 atü of water gas are pressed on and heated up. Starting with 150°, feed stock (400-450 l/hr) is put through, while the temperature is gradually raised to 215°. At this temperature the conversion rate was 40%, the methane formation high (Mv = 25). On raising the temperature still more, the conversion rate rose to U = 54 (Mv = 12). A higher conversion rate could not be attained, although the temperature rose to 222°. The experiment was terminated, for this reason. The reactor was easy to discharge.

Evaluation of the catalyst

Slight activity. Mediocre conversion rates (U = 50) in the 215-222° range, with Mv = 12 and X = 0.6.

M. Beth

SINCLAIR REFINING COMPANY

1721

May 1, 1947

Reel 42
Bag 3439-22
Page 424

S-63.

Oberhausen-Holten
January 27, 1944

Experiment 650

100 Fe, 5 Cu, 10 CaO, 5 kgr (soda precipitation) 3% KOH-impregnation

Hot nitrate solution (42 kg of Fe-nitrate, 1.75 kg of Ca-nitrate, 1.17 kg of Cu-nitrate, 120 l of water) is introduced into boiling soda solution (24 kg of soda, 120 l of water). 0.35 kg of kieselgur are added. After stirring it for a short period of time, filtration through the filter press. Washing with hot condensate (30 minutes). Drying with air (15 min.). The catalyst cake is treated three times with 500 l of condensate each time in the settling vat. Filtration through filter press, washing (10 min.) and drying. For the purpose of alkali impregnation, the catalyst cake is passed through the fiber press adding potassium hydroxide (0.21 kg of KOH, 1 l of water). Spreading the cake on trays, drying in the drier at 140°. Forming 1-3 mm granules.

Reduction in the 6 ltr. reductor (R25a)

5 l of "Gruenkorn" are introduced into the nitrogen filled apparatus. 28 m^3/hr of H_2N_2 (75% H_2) are passed through at 325° during 24 hours. Cooling with O_2-free N_2 (reacted with CO-mixed catalyst) during one hour. Discharging under nitrogen. Shrinkage 30%; heaping weight 780; Fe density 726; reduction value 85%.

Testing the catalyst in the reactor MR1

4.47 kg (about 5 l) are introduced into the reactor. Slow heating up while a slight quantity of feed stock is put through under 10 atü of water gas. At 140° the first reaction was observed and a CO consumption of approximately 31% was observed. Up to 155° only CO was consumed (about 40%). In the 160-180° range the hydrogen began gradually to participate in the conversion. The methane formation remained below 1%. The conversion rate rose to about 40%. By gradually raising the temperature still more, after 50 hours of operation at 205° a conversion rate of 65% could be achieved. (Mv = 13; X = 0.67). This conversion rate could be kept constant at a temperature of 206° for the next one hundred hours of operation, without a substantial increase in the methane formation (Mv = 18). Thereafter, however, heavy methane formation started suddenly (Mv up to 76). When the methane formation failed to decrease after 16 hrs. and the feed stock passed under great resistance, the test was terminated. By the carbon deposit which had occurred, the discharge was difficult.

Evaluation of the catalyst

Fair conversion rate at low temperature (206°; U - 65; Mv = 18; X = 0.65). Very strong tendency towards increased methane formation and carbon deposit. Because of spontaneously occurring overheating, not to be controlled in the reactor.

M. Both

SINCLAIR REFINING COMPANY

1122

May 1, 1947

Reel 42
Bag 3439-22
Page 425

S-64

Oberhausen-Holten
January 28, 1944

Experiment 657

100 Fe, 5 Cu, 10 CaO, 50 kgr (potash precipitation)

Preparation of catalyst F2201 in the laboratory

0.3 kg of kieselgur is treated with boiling potash solution (29 kg of potash, 190 l of water) for one minute. Hot nitrate solution is introduced (36 kg of Fe-nitrate, 1.5 kg of Ca-nitrate, 1.0 kg of Cu-nitrate, 120 l of water). Admixing 2.7 kg of kgr. After a short period of stirring filtration through a filter press. Washing with hot condensate (30 min.). Drying with air (15 min.). Spreading the catalyst cake on trays. Drying in the drier at 140°. Forming 1-3 mm granules.

Reduction in the 6 ltr. reductor (R12)

6 l of "Gruenkorn" are introduced into the nitrogen-filled apparatus. 35 m^3/hr of N_2H_2 (75% H_2) are passed through at 180° for 24 hours. Cooling down with O_2-free nitrogen (treated with a CO-mixed catalyst) during one hour. Discharging under N_2. 16.7% shrinkage; heaping weight 426; Fe density 163; reduction value 93.5%.

Testing the catalyst in the reactor MR1

1.94 kg (about 5 l) are introduced into the reactor. Slow heating up, while slight feed stock quantities are put through under 10 atü water gas. Starting with 165° full feed stock through put (500 l/h). At 195° for a short period of time much methane was formed. At 210° a conversion rate of 88% (Mv = 15) was attained. Further increase in temperature to 218° failed to raise the conversion rate beyond 45% (Mv = 16). After a short period of time the conversion rate dropped so much that there was no use in continuing the experiment.

Evaluation of the catalyst

In spite of rather high temperatures poor, quickly decreasing conversion rates (218°: U = 45; Mv = 16; X = 0.67).

M. Beth