SINCLAIR REFINING COMPANY

1728

5-69

May 5, 1947

Reel 42
Eag 3439-28
Page 650

Ruhrbenzin A. G.
Oberhausen-Holten, June 3, 1939

Re: Neutral-oil separation from the Diesel-addition products.

I mentioned already in my letter of February 8, 1939, that it might be possible to obtain neutral-oil free Diesel- addition products (Dieselanlagerungsprodukte) by cutting the Diesel oil used as parent material into sufficiently narrow fractions and by separating thereafter the mixture of additives by means of distillation in vacuo. We have applied this method only at the preparation of fatty acids, up till now, but we were successful therein.

The nature of these synthetic fatty acids makes it impossible to use them technically, up to this date. But that may not apply to higher-molecular alcohols obtained by the addition of water gas. That is why I am requesting you to make preparations for the production of larger quantities of Diesel alcohols in accordance with this procedure. That is, the olefin-containing Diesel oil used as a starting material would have to be split up in so narrow fractions that the highest boiling neutral portions have still a lower boiling point than the lowest alcoholic portions.

The actual experiences concerning straight-chained materials seem to indicate that the differences in the boiling points between the alcohols and the hydrocarbons are not important, especially not in regard to the higher molecular hydrocarbons. But considerable differences seem to exist in the melting points, therefore, the aforementioned procedure for preparing pure higher alcohols could also be conducted in such a way that the olefin containing hydrocarbons are once more separated into narrow fractions, but that these fractions are frozen out, instead of distilling them in the vacuum, and that the neutral oil is separated by filtration from the frozen alcohols.

M. Beth

SINCLAIR REFINING COMPANY

L729

May 5, 1947

Reel 42
Bag 3439-28
Page 652

S-70

Dr. Landgraf

Re: Olefin-carbon-monoxide addition

We ought to find out experimentally whether the cobalt which is dissolved in our reaction products prepared by the ~~carbon-monoxide-ethylene addition, can have catalytic~~ effects also in this form.

We ought to start this study by preparing a liquid product with a maximum cobalt content. This product must be filtered and introduced into the autoclave. Then, we would have to find out whether an ethylene-water gas mixture undergoes a reaction on being passed through, or whether the presence of solid catalysts is necessary for this purpose.

Roelen

M. Beth

MB:hlm

SINCLAIR REFINING COMPANY

1730

May 5, 1947

S-71

Reel 42
Bag 3439-28
Page 653-4

Oberhausen-Holten
November 15, 1939

Dr. Landgraf

Re: Aldehyde-Oxydation

I

A decrease inyields will not necessarily result from water being incompletely added to Diesel-olefins, becasue the olefin-containing neutral-oil may either be used as Diesel-oil, or may be recycled to the addition reactor.

However, the incomplete oxidation of the aldehydes is to be considered as a loss, because the aldehydes cannot always be left in the Diesel-oil. Therefore, we must try to obtain the maximum oxidation rate for the aldehydes.

We must try hard to achieve this goal, since all the neutral oils, which are actually prepared, are still containing a considerable percentage of aldehydes.

II

The following methods may be studied in regard to attaining a more complete aldehyde oxidation.

1. Increasing the residence period.
2. Operating at higher temperatures.
3. Increasing the oxygen concentration, starting with air and proceeding to pure oxygen.
4. Increasing the pressure, using air, resp. oxygen under higher pressure.
5. Using oxygen transmitters, such as salts of manganese, etc. or the catalysts employed at the paraffin oxidation.
6. Oxidation in the presence of lye, currently removing the acids formed from the aldehyde-containing oil.
7. Maximum contact between oxygen and oil, e.g., by means of mechanical stirrers (turbo-stirrers) or in a different manner.
8. Oxidation (not with molecular oxygen) but with chemicals e.g., with substances which easily give off oxygen, such as higher oxides of manganese, etc., H_2O_2, if necessary, in an alkaline solution.

9. Recycling the oxidated, lixivated, however still aldehyde-containing oils to renewed oxidation.
10. Simultaneous use of the various measures in question, the purpose of enhancing their effect.

Poelen

M. Beth

MB:hlm

SINCLAIR REFINING COMPANY

1732

May 2, 1947

Reel 48
Bag 3439-88
Page 8554

S-72

Oberhausen-Holten
November 25, 1938

Dr. Landgraf

Re: Preparation of low boiling olefins

On October 17, 1938, I suggested to try the preparation of low-boiling olefins by means of a diluted catalyst at high temperatures and under high pressures.

An actual experiment failed. We obtained preeminently methane and, furthermore, only low conversion rates.

At the present time, I am suggesting to repeat this test, but this time with a carbon dioxide-containing water gas. This mixture of our stock ought to have the following effect:

The carbon-monoxide excess shall suppress the methane formation, whereas the presence of carbon dioxide shall prevent the splitting of carbon monoxide into carbon dioxide and carbon. For example, we may run the test with water gas containing 20% of carbon dioxide, 250-450°, pressures up to 1000 atm., cobalt, thorium, magnesium upon purified kieselgur, the cobalt being of slight density.

It is feasible that we may be successful only by using a particularly suitably proportioned mixture. For this reason, experiments ought to be conducted with a different mixture than the aforementioned, that is, with stock containing more carbon monoxide than would correspond to the ratio/CO to 2Hg, and furthermore containing larger quantities of carbon dioxide. Finally, one may consider recirculating the carbon dioxide and reacting small quantities of fresh water gas each time. In this connection, it will be interesting to learn, at what concentration the carbon dioxide begins to oxidate the metallic cobalt in the presence of carbon monoxide and hydrogen to an appreciable extent.

Roelen

MB:hlm

M. Beth

SINCLAIR REFINING COMPANY

1733

May 2, 1947

S-73

Reel 42
Bag 3439-28
Page 657

Oberhausen-Holten
November 18, 1938

Dr. Landgraf

Re: Fatty-acid Production

With our actual methods for preparing fatty acids from olefin-containing Diesel-oil, we obtain yields of about 50% based on the olefins contained in the parent oil.

It must be found out, what substances are contained in the recovered neutral oil (combustion, etc., its contents of aldehydes, alcohol, non-converted olefins).

In the most-favorable cases, the olefin portion which has not been converted into fatty acids, will remain unreacted. Then, it would be possible to have the neutral oil recovered from the first working-up, react another time with water gas. In this way, it would be possible to enhance the yields quite considerably. Please, run this test without delay. It will be suitable to find out first, in the stirrer autoclave, how much water gas has been converted.

If we fail to obtain a satisfactory reaction by this operation scheme, in spite of the analysis showing a sufficient olefin content, we would have to consider the possibility that catalyst poisons are contained in the recycled neutral oil. Such poisons might be residues of alkalies, fatty acids, etc. If necessary, the neutral oil would have to be suitably purified before being fed for a second time.

Roelen

M. Beth

MB:hlm

SINCLAIR REFINING COMPANY

1134

S-74

May 2, 1947

Reel 42
Bag 3439-28
Page 658-9

Oberhausen-Holten
December 9, 1938

Dr. Landgraf

Re: Diesel-oil condensation

1. On adding water gas to Diesel olefins we found:

a) CO and H_2 are taken up in a 1:1 ratio.
b) The taking-up stops when, in accordance with their order of magnitude, as much oxygen has been taken up as has been calculated for the complete conversion of olefins into aldehydes.
c) The iodine number drops practically to zero.

Therefrom, we may conclude that essentially aldehydes (resp. ketones) have been formed.

2. Up to this date, we tried to work-up A-oils in both of these two schemes:

a) Preparing pure aldehydes. Up to this date, we failed in obtaining them, because we did not yet succeed in separaring the bisulfite compounds from the Diesel aldehydes.
b) Oxidation of the aldehydes to fatty acids. The oxidation is easy. But because of the prevailing analytical difficulties, the reaction could not yet be evaluated quantitatively.

3. Now I am suggesting to work-up the A-oils by means of hydrogenation to alcohols and subsequently to esters. Thereby, we should gain a more intimate understanding of the reaction as well as new products.

a) The hydrogenation could directly succeed the water gas addition in the autoclave. Water gas is to be discharged, hydrogen is to be pressed on.

We shall have to find out what temperature is most suitable for a hydrogenation to alcohols.

The reaction will have to be followed by an analytical determination of the OH-number (by means of acetic-acid anhydride, or by means

of the Grignard-reagent), of the decrease of the aldehyde contents, as well as of the H_2 - uptake.

We might also start by continuously adding water gas, and later on, we might hydrogenate the stock in an autoclave, using a fresh catalyst. In this case, however, the A-oil would have to be protected against air during the transfer stage.

b) The mixture of Diesel alcohols and neutral oil which we obtained, can be esterified with carboxylic acids.

If we use benzine fatty-acids, we may expect to get amylacetates.

On using our Diesel fatty-acids, high molecular esters are to be expected. It will be interesting to learn what properties they will have.

Probably their boiling points will be so high that it will be possible to distill off the neutral oil in the vacuum.

In regard to the size of their molecules these "Diesel-esters" ought to be already of a wax-like character, like bees-wax, for instance. (The latter one contains also ketones and hydrocarbons.)

But it may also happen that from the alcohols, resp. from the higher Oxe-compounds, e.g., the esters, lube-like materials will be formed, be it by esterification with their own acids, or in some other manner.

For the purpose of esterification, e.g., to the hydrogenated alcohol-neutral oil mixture, the calculated quantity of Diesel fatty acid is added and a small quantity of hydrogen chloride, about 3-5%. The total mixture is heated for a longer period of time at the reflux cooler, until the free fatty acid disappears. Finally, the neutral oil and the hydrochloric acid are distilled off.

Roelen

M. Beth

SINCLAIR REFINING COMPANY

May 2, 1947

I-T-C-O

1736

Reel 42
Bag 3439-28
Page 660

S-75

Oberhausen-Holten
December 30, 1938

Dr. Landgraf

Re: Side reactions at the addition

It is well known that our addition-products contain by-products along with primary aldehydes. As far as we can find out at this time, this is the more true the smaller the sizes of the parent olefins. Accordingly, ethylene yields only 30 to 50% of propyl aldehyde, whereas the Diesel-olefins practically yield nothing but aldehydes. This phenomenon may be probably explained by the fact that the low aldehydes formed by easily continue to react under the conditions of their formation.

In order to gain further information about this phenomenon, we ought to subject aldehydes to the addition-reaction conditions separately, in presence of one of the various reaction participants. In this way, we should find out, for instance, whether the well known disproportionation of aldehydes into acids and alcohols, resp. esters, will occur.

Then, we should try to learn in which manner the primary reaction product, namely, the aldehyde, participates in further reactions.

1. With hydrogen; formation of alcohols. This reaction has already been studied.
2. With olefins, possibly forming ketones. This reaction has to be studied.
3. With carbon monoxide. Actually we do not know what reactions will occur. They must be studied.
4. With itself: either disproportionation (esterification) or condensation to higher molecular products. This phenomenon would have to be studied. If necessary, in the nitrogen stream.

Roelen

M. Beth

MB:hla

SINCLAIR REFINING COMPANY

1737

May 5, 1947

S-76

Reel 42
Bag 3439-28
Page 662-3

Oberhausen-Holten
October 28, 1938

Dr. Landgraf

Re: Alcohol formation at the aldehyde synthesis

Our fatty acids are said to contain appreciable quantities of hydroxyl groups. Regardless, whether these findings will be confirmed or not, larger quantities of alcohols have been found in our lower-boiling condensation products, in the benzines prepared under higher pressures, and finally, in Fischer's synthol.

We may assume that they were generated by hydrogenating the aldehydes. Without any doubt, the same side-reaction, that is, the hydrogenation of aldehydes to form alcohols, can also occur in our vapor-phase or liquid-phase aldehyde-synthesis. There is no reason to be seen, why the aldehydes should not be hydrogenated by the water-gas hydrogen in presence of the cobalt catalyst.

Therefrom may be deduced that the aldehydes must be removed from the reaction area without delay when we aim at attaining maximum yields of primary aldehydes, in order to avoid the effect of the hydrogen. When we apply the continuous operation in the vapor phase, they are currently removed.

A particular disadvantage in this respect is offered by applying the discontinuous operation in the liquid phase. It is feasible that the Diesel-oil olefins would be converted exclusively into alcohol, if they were reacted in the autoclave with water gas, until there is no more pressure drop.

Obviously, this procedure is quite unsuited for the fatty-acid synthesis as we are planning it. Therefore, we must try to condense also the high-molecular olefins with water gas in the continuous operations; this can be easily done in various ways. At the same time, these considerations explain the reaction mechanism in forming alcohol from carbon-monoxide and water.

(Signature illegible)

M. Beth

SINCLAIR REFINING COMPANY

1738

May 2, 1947.

Reel 42
Bag 3439-28
Page 672

S-77

Oberhausen-Holten
December 30, 1938

Dr. Landgraf

Re: Ketone formation

Already when we started our high pressure experiments, I suggested to study the formation of ketones by reacting ethylene with aldehydes. We ran such a test, using acetaldehydes. Its result was conclusive. However, only a single test had been made at that time; and furthermore, we ought to consider that because of its low boiling point, acetaldehyde is not quite suitable for solving this problem.

I am therefore requesting you to take up these experiments once more, and to run some tests with higher aldehydes. For instance, we might use propyl aldehydes or, most expediently, benzine aldehydes, resp. the still higher boiling Diesel aldehydes. The higher the boiling point of the aldehydes, resp. of the liquid, the easier it would be to recognize a drop in the ethylene pressure curve, if any.

The test should be run in the usual manner in the upright stirrer-autoclave at rising temperatures and in the presence of our cobalt catalyst.

Roelen

M. Roth

MB:hlm

SINCLAIR REFINING COMPANY

1739

May 2, 1947

S-78

Reel 42
Bag 3439-28
Page 673

Oberhausen-Holten
December 30, 1938

Dr. Landgraf

Re: Preparation of fatty acid via alcohols

Our experiments showed that by oxidating aldehydes, not all of them are converted into fatty acids, but that a considerable part of the aldehydes refuses to be converted into fatty acids.

Perhaps, these and other difficulties occurring in the aldehyde oxidation, could be avoided by first hydrogenating aldehydes so that they form alcohols, and by subsequently oxidating these alcohols into acids. Although this method may appear to be clumsy, for completeness' sake it ought to be tested at least once.

M. Beth

MB:hlm

SINCLAIR REFINING COMPANY

1740

May 2, 1947

S-79

Reel 42
Bag 3439-28
Page 671-72

Oberhausen-Holten
December 13, 1938

Dr. Landgraf

Re: Program concerning addition-issues

A) Working-up of fatty acids

1. Preparation of neutral-oil-free acids.
2. Ascertaining their properties, esp. the quantity of OH constituents.
3. Vacuum distillation of the acids at 3 mm.
4. Saponification of a sample, testing its smell and trying to remove it.

B) Preparation of new fatty acids, 2. series

1. These experiments are aimed at preparing as pure acids as possible on the basis of our prior experiences.
2. At first, tests are to be run in regard to the limitation of the water-gas addition in the formation of aldehydes, while avoiding to hydrogenate them to form alcohols.
3. The A - oils which will be thus obtained will be oxidated under the most favorable conditions known. At this time, that means: Oxidation under mechanical stirring, without diluting the oil with water or alkali, paying special attention to the temperature which ought not rise much above 20° C.
4. Experiments concerning the possibility of removing the side reaction higher alcohols from a soap solution by extracting them with benzine and alcohol. The alcohol containing soap solutions can be easily prepared by adding dehydrogenated A-oil.
5. After these preliminary tests, preparation of pure fatty acids of series 2.
6. Ascertaining the properties of these acids.

C) Preparation and examination of fatty acids which can be prepared from primary Diesel-oil by means of lyes.

D) Preparation of about 1 liter of Diesel alcohol for transfer to the Analytic Institute, if necessary from the 260-320° fraction.

MB:hlm

M. Both

SINCLAIR REFINING COMPANY

1741

Reel 42
Bag 3439-28
Page 679

S-80

January 3, 1939

Dr. Landgrof

Re: Additions

It would be worthwhile to find out whether the temperature limits prevailing for the three individual reactions (olefin hydrogenation, water gas addition, aldehyde hydrogenation) vary when nickel or iron catalysts are used instead of cobalt catalysts. This would be particularly interesting in regard to nickel because of its greater hydrogenation capacity.

These results might be useful when the addition products are to be hydrogenated so as to form alcohols.

Roelen

M. Beth

MB/BH

SINCLAIR REFINING COMPANY

Reel 42
Bag 3439-28
Page 680

1742

S-81

February 8, 1939

Dr. Landgrof

Re: Neutral-Oil Separation from the Diesel Aldehydes

Since the prior attempts at preparing Diesel aldehydes in pure form were more or less a failure we ought now to try separating them by high-vacuum distillation.

It would be an advantage, first, to separate the olefin-containing Diesel-oil into so narrow fractions that afterwards a sufficient difference in the boiling temperatures of neutral oil and oxygen-containing constituents might be obtained. In view of the fact that after preparing raw acids and fatty acids, we are used to fractionating the fatty acids anyway, the working-up of olefin-containing Diesel oil into individual fractions would not mean too much additional work.

To be sure, if this method should prove successful, we should be in the position to prepare larger quantities of aldehydes and also larger quantities of fatty acids in a simple way.

Roelen

MB/BH

M. Beth

SINCLAIR REFINING COMPANY

Reel 42
Bag 3439-28
Page 681

1743

S-82

Oberhausen-Holten
February 7, 1939

Dr. Landgraf

Re: Synthesis of Acids and Ketones

It is well known that our freshly reduced catalyst is oxidated by water already at a temperature of 100° and less, to such an extent that after some length of time the cobalt can be perfectly converted into an oxide.

Thus, on slowly heating up ethylene and carbon monoxide together with water and a freshly reduced catalyst, the catalyst may be oxidated by the water before the desired synthesis gets under way.

Therefore, we may try to suspend the catalyst in an oil emulsion to heat it up to the reaction temperature together with ethylene and carbon monoxide, and to add thereafter currently small quantities of water, corresponding to the water consumption. An alternative would consist in operating continuously with a moistened mixture of ethylene and carbon monoxide.

Roelen

MB:ep

M. Beth

SINCLAIR REFINING COMPANY

Reel 42
Bag 3439-28
Page 682-4

1744

S-83

Ruhrbenzin A.G.
February 6, 1939

Dr. Landgraf

Re: Synthesis of Acids and Ketones

I.) On adding water gas to olefins, especially to ethylene, we could clearly ascertain two temperature ranges yielding different reactions:

Below 100°, ketones are formed as side reactions; above 100° the aldehydes are hydrogenated to form alcohols and the olefins will form saturated hydrocarbons.

The mechanism of the alcohol-forming reaction is quite clear; the ketone formation, however, is by no means perfectly clarified.

Now, I should like to point out that simultaneously with the ketone formation we observed also the appearance of acids. For instance, from ethylene noticeable quantities of propionic acid were formed along with propylaldehyde and diethylketone. I am assuming that we are here confronted with certain correlated phenomena, which might clarify how the ketone forming reaction takes place.

II.) It has been known for a long time that from the calcium salts of the fatty acids the corresponding ketones are formed by dry distillation. Furthermore, fatty acids are converted into the corresponding ketones by catalytic decomposition, especially, on passing their vapours over suitable catalysts, whereby carbon dioxide and water are liberated.

On assuming that somehow propionic acid is formed, the subsequent formation of the diethylketones may be understood without difficulty, this being a well known reaction.

It is still unclear, in what way the acid would be initially formed. It is well known that two mols of aldehydes can change their structure (Sich um lagern) into alcohol and acid in the presence of alkalies with water. If this reaction would be the basis of the acid form and, thereby, of the ketone formation, we should always find a corresponding quantity of alcohol along with the ketone, and that, in the molecular proportion of two alcohols to one ketone. This, however, has not been observed. Therefore, we may assume that with our synthesis, this type of reaction fails to take place to an appreciable extent.

It is theoretically feasible that acid formation may occur, when water (instead of oxygen) is added to the olefin along with carbon monoxide. This assumption could easily be checked by reacting a mixture of ethylene, carbon monoxide and water, if necessary in the presence of hydrogen.

Now, our normal synthesis mixture does not contain any water. Thus, the acid formation in question cannot occur by itself. Particularly, appreciable quantities of ketones could not be formed.

We may, however, assume that through some side reaction small quantities of water are formed, e.g., by carbon monoxide reduction. This would also be consistent with the experimental test insofar as we have always found some water in our reaction samples. When once water is present, the acid formation in question can occur.

Since the condensation of two mols of acid to one mol of diketone takes place under the liberation of carbon dioxide and water, even a comparatively small quantity of water can effect the formation of a larger quantity of ketones by being converted over and over again, whereby at all times the actual concentration of the free acid will be a low one.

These relations are somewhat consistent with out experimental findings; therefore, we ought to find out whether we can enhance the formation of acid, resp. ketones, by adding ~~water to the mixture of ethylene, carbon monoxide and hydrogen,~~ resp., by substituting water for hydrogen.

III.) In this manner it might be possible to produce larger quantities of acids, resp. of ketones in one operation, starting from olefins. However, we ought to find out first, whether it is not more suitable to aim at preparing aldehyde, resp. alcohol, first, then to oxidate it to acid and finally to convert the acid vapours catalytically into ketones; for such a multiple-stage operation speaks that the reaction conditions can be exactly regulated for each type of conversion and that we may perhaps avoid some side reactions. The oxidation might be effected quantitatively. The ketone formation from acids gives a 90-95% yield.

On the other hand, the single-step operation offers the twofold advantage of being simple and saving material, because hydrogen would not be consumed.

IV.) Since water is liquid, not gaseous, under pressures of 100 ats. we may plan to conduct the synthesis of acids, resp. ketones in such a way that the catalyst is suspended in water and that ethylene and carbon monoxide are stirred in under pressure.

Another method would be to operate continuously and to have the water drop through the catalyst layer in the well known manner, while ethylene and carbon monoxide are passed through at the same time.

V.) On using higher olefins, the catalyst could be suspended in a stoichiometrical mixture of the liquid olefins and water, and then carbon monoxide could be stirred in under pressure and at higher temperatures. In this way fatty acids would be formed from Diesel oils in a single step.

Roelen

FB:op

F. Beth

SINCLAIR REFINING COMPANY

Reel 42
Bag 5439-28
Page 685

1747

S-84

Oberhausen-Holten
January 30, 1939

Dr. Landgrof

Re: Carbon-Monoxide Addition to Diesel-Olefins

Hitherto, our attempts to form fatty acids by adding carbon monoxide to Diesel olefins have shown that the acids obtained are probably of a branched-chain structure, having low congealing points for this reason.

It is feasible that less complex branched-chained acids could be obtained, if we should not start from the primarily formed synthetical hydrocarbons, but from hydrocarbons obtained by splitting them off from the corresponding higher synthetical fractions. We may namely assume that the side-chains are being split off, so that the splitting products will be of a more straight-chained structure than the average primary products of equal molecular size.

I am therefore suggesting to prepare an olefin-rich Diesel-oil by splitting paraffin resp. hard paraffin, and to use this oil for additions, resp. fatty-acid oxidations.

Suitable conditions for the splitting distillation are described, for instance, in the work published by Vonnen and myself on November 19, 1937.

Roelen

MB:op

M. Beth

SINCLAIR REFINING COMPANY

1748

S-85

May 5, 1947

Reel 42
Bag 3439-28
Frame 688

Oberhausen-Holten
January 30, 1939

Dr. Landgraf

Re: Olefin-addition

We ought to try to add water gas to the conversion products obtained by reacting hydrocarbons with aluminum chloride, etc.

For instance, an olefin-rich lubricating-oil fraction could be procured from the main laboratory, and then the addition could be prepared in the usual manner, followed by reduction or oxidation.

Roelen

M. Beth

MB:hlm

SINCLAIR REFINING COMPANY

1749

May 5, 1947

S-86

Reel 42
Bag 3439-28
Page 689

January 17, 1939

Dr. Landgraf

Re: Working-up the ethylene-addition product

The ethylene production product ought to be worked up in the following manner:

1. Separating the propylaldehydes and the diethylketones

These substances being the most desirable products for us, the working-up process must be primarily aimed at smoothly obtaining both of these compounds. For instance, we could distill them off under normal pressure (up to approximately 135°C) as we have already succeeded in doing. Whether the distillate shall be finely fractionated or not, depends upon the quantities desired and the column available.

In order to prevent the formation of that hitherto unanalyzed decomposition product which boils at 80°C., we might also conduct the distillation at a more or less decreased pressure.

2. Working-up of the distillation residue

Pursuant to our experiences, the distillation residue of more than 130° cannot be worked-up under normal pressure. Thus, one might try to distill the recovered distillation residues of more than 130° either by means of a simple vacuum distillation without fractionation, or by means of a very careful heating up. But we might also try cautiously to hydrogenate the distillation residues, with or without vacuum distillation. It is feasible that by this process useful, although stable compounds may be prepared. One might also conduct an exhaustive hydrogenation operation inorder to be able to draw conclusions from the hydrocarbons formed upon the previous oxygen-containing compounds.

Roelen

M. Beth

SINCLAIR REFINING COMPANY

1750

May 5, 1947

S-87

Reel 112
Bag 3439-28
Page 690

January 17, 1939

Dr. Landgraf

Re: Separation of aldehydes

We did not succeed in separating the higher aldehydes from the neutral oils although, e.g., the additive compounds with bisulfite are most readily formed.

Perhaps, they could be separated by first subjecting the mixture consisting of the bisulfite compound and of the neutral oil to a vacuum distillation.

In doing so, it would become unnecessary to remove all the neutral oil; on the contrary, complete elimination would have to be avoided in the interest of a favorable heat transfer and, sometimes, additional neutral oil of the right boiling-point range must be added. Indeed, the vacuum distillation is aimed at removing the water. There is namely, some reason in assuming that there will be no trouble at the washing with benzine caused by the formation of unseparable emulsions, when water will be absent.

The process might be conducted for instance, in such a way that the raw product is first reacted with a bisulfite solution. Then, the major part of the aqueous solution is separated. This pasty mixture is mixed with an appropriate quantity of a heavy-oil fraction of e.g. 200-250°C., sufficient for the heat transfer during the vacuum distillation. By means of an oil bath all the water is thereafter removed in the vacuum. Subsequently, we ought to be able to separate the bisulfite compound from the neutral oil by means of a simple filtration process as well as by means of a benzine wash.

M. Beth

MB:hlm

SINCLAIR REFINING COMPANY

1751

May 5, 1947

5-88

Reel 42
Bag 3439-28
Page 691

Oberhausen-Holten
January 11, 1939

Dr. Landgraf

Re: Olefin with water-gas addition in recycle
conf. my letter of Nov. 18, 1938

As mentioned before, we are going to try to enhance the yields of primary aldehydes by working with recycle. The quality of the composition of the recycle stock is thereby of importance. For instance, on working with ethylene and water gas the following four fundamental possibilities exist:

a) Stoichiometrical mixture
b) Much ethylene, little water gas
c) Little ethylene, much water gas
d) Many inerts, little ethylene + water gas.

It will be expedient to provide for a low concentration of those constituents, which might cause side reactions. This is probably the water gas.

It is hardly to be assumed that ethylene alone would react under the addition conditions; but at the actually used temperatures water gas alone might react. On circulating much ethylene and little water gas, the optimum conditions for the formation of aldehydes may be given.

Since for the time being we may not count on getting a compressor we could test these ideas in a once-through test, and at that, for both the cases B) and C).

The actual methods for treating diesel olefins corresponds already to the aforementioned concentration ratio of much olefin and little water gas. It seems that in this case the aldehyde yields are proportionately larger than with the ethylene-water gas addition from an approximately stoichiometrical mixture.

Roelen

M. Beth