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## FUEL MANUFACTURE

### Catalytic Cracking of Petroleum Fraction

For the purpose of designing, obtaining the data for construction, and determining the operative conditions of petroleum catalytic cracking equipment, the semi-commercial experimental installation was established and the various experiments have been performed, the catalyst being the Active clay. It was proved that of the various kinds of reaction columns examined, i.e. those of centre tubular, fused salt circulation, long tubular hollow types the last mentioned is convenient in construction and good in function.

### Hydroreforming of Catalytically Cracked Gasoline

The hydroreforming has been studied as the aftertreatment for the catalytically cracked gasoline, whereas the catalytic reforming or the sulfuric acid treatment was proved to be rather more convenient for the present purpose, the large scale practice of the hydroreforming being accordingly stopped.

The results of investigation can be outlined as follows:

1. Reaction conditions.  
Press. 20Kg/cm<sup>2</sup>    Temp. 150 - 200°C    Space Velocity 1
2. When the catalytically cracked gasoline is treated under the foregoing conditions, the unsatd hydrocarbon in the gasoline can be decreased to ca 0.1% the Sulfur being almost completely removed.
3. Catalyst used.  
The Ni:Acid clay (1:1) catalyst used was proved to have a short life, and the octane value and the lead effect was not so elevated as expected later on together with the improvement of the cracking method, the catalytic reforming or the simple sulfuric acid washing was found more recommendable for the purification of the catalytically cracked gasoline, the studies line were stopped.

### Study on High Pressure Hydrogenation Of Petroleum Naptha Fraction

The molybdenum trisulfide fabricated has been examined for the pressure hydrogenation of petroleum Naptha fraction with the following results.

Catalyst	MoS <sub>3</sub> Alone	MoS <sub>3</sub> -Acid clay
Oil velocity	1L/hr	"
Hydrogen velocity	1000 L/hr	"
Space velocity	%	"
Yield of aviation gasoline	40 - 50 %	50 - 60 %
Octane Rating of Aviation Gasoline on 0.1 vol% leading	89 - 90	90 - 91
Remark	Marked Decrease in activity is observed in the first period.	The catalyst has a long life.

## Catalytic Cracking of Acetone

Acetone was anticipated to be abundantly obtained as the byproduct of the butanol fermentation.

For the purpose of fabricating isooctane from this byproduct acetone, the fabrication of isobutylene by the catalytic cracking of acetone has been studied. The process was at first fundamentally examined in the laboratory scale and then with the semi-commercial experimental plant.

The results obtained are summarized as follows:

Catalyst	ZnCl <sub>2</sub> Carrier Active Carbon	S <sup>1</sup> / <sub>2</sub> WO <sub>3</sub> Carrier Aluminium Silicate	Active Clay
Reaction Apparatus	Multitubular Catalyser, outside Heat Transfer Area 25 m <sup>2</sup> /m <sup>3</sup> Heating Medium Dosam A Biphenyl Ether 75% Diphenyl 25%	Box Type Heat Transfer Area 15 m <sup>2</sup> /m <sup>3</sup> Heating Medium Hot Air	Adiabatic Cylinder Type Heated to Reaction Temp. with Superheated steam at Start.
Reaction Temp.	280 - 300	400 - 450	450
Space Velocity	0.05	0.1 - 0.2	0.3 - 0.5
Life of Catalyser	15 - 20 Days	8 hrs.	30 mins.
Regeneration Of Catalystr	Impossible	Can be regenerated with Hot Air and Steam (Maintaining O <sub>2</sub> Content) 3-4%	30 mins.
Isobutylene Yield	To Aceton Charged 15% To Aceton Converted 25%	To Aceton Charged 15% To Aceton Converted 25%	To Aceton Charged 20% To Aceton Converted 25%
NOTE	Large Quantity of Acetic Acid formed	Large Amount of Mesitylene formed. Acetic Acid small.	Large Quantity of Acetic Acid formed.

## Manufacture of Isooctane from Butanol

On passing butanol through the phosphoric-acid Kieselguhr catalyst at 300 - 350°C, with the liquid space velocity 0.1 - 0.2, the dehydration occurs together with the isomerization, giving the butylene gas mixture containing 30 - 40 % of isobutylene. This gas mixture is polymerized by passing it through the phosphoric acid-kieselguhr catalyst at 150 - 200°C with the liquid space velocity 0.5 - 2 to isooctane, which is hydrogenated at 180 - 230°C with the Nickel kieselguhr catalyst to isooctane, the throughout yield being 45 wt % against butanol and the life of catalyst about one month.

## Studies on Aromatization

For the purpose of elevating the octane rating of the low octane inferior crude or synthetic petroleum fraction, the aromatization in a commercial scale of such fraction with catalysts containing chromium, alumina and etc., was undertaken and an experimental installation in a semi-commercial scale was under construction. It was abandoned however, on the way of construction owing to the sudden change of national situation.

## Manufacture of Aviation Gasoline From Soja Bean Oil By High Press. Hydrocracking

The high press. Hydrocracking of Soya Bean Oil gives an aviation gasoline in an yield of 35 - 40 %, the life of catalyst was proved to be at least over 20 days.

The results obtained are summarized as follows;

Raw material oil	Soja bean oil
Catalyst	Molybdenum Trisulfide
Oil velocity	500 c.c. per hr.
H <sub>2</sub> Velocity	2000 l. per hr.
Liquid space velocity	0.5
Duration of operation	16 Days
Yield of Aviation Gasoline	34 - 40 %

## Manufacture of Aviation Gasoline From Rubber

Continuing to the laboratory experiment with the Autoclave the manufacture of aviation gasoline thro the hydrocracking of rubber has been studied in the pilot plant with the following results.

### 1. Two stage Hydrogenation

Crude Rubber depolymerised and liquified by submitting it to the depolymerisation at 280 C under elevated steam press is hydrocracked in the liquid phase with the flowing catalyst, the middle oil thus obtained being hydrogenated in the vapor phase to the aviation gasoline.

2. Thermal Cracking - Hydrogenation  
Crude Rubber depolymerised and liquified at 280°C under ordinary press is thermally cracked at 420 - 450°C. the middle oil obtained being hydrogenated in the vapor phase with the Mo catalyst to the aviation gasoline.
3. Octane values of aviation Gasoline thus obtained by the first Method by the Second Method
 

0.15 Vol % Leading	91
" "	95

### Catalyst for Fischer Petroleum Synthesis

As a relief mean for the deficiency of cobalt required by fabricating the catalyst for the Fischer petroleum synthesis the use of iron catalyst is taken into consideration. The iron catalyst can be used when the furnace is so reconstructed that the temperature for synthesis may be elevated. A concrete plan for fabricating this catalyst was in progress when there occurred such difficulties as hopelessness for obtaining a large amount of nitric acid required, impossibility for preparing a stainless steel tank for dissolving with nitric acid and so on. Fortunately the yellow mud (natural Iron Oxide) is considerably found in various districts of Japan and the consumption of nitric acid can be saved to a greater extent by using this mud.

The experiment has been performed with the catalyst prepared from the yellow mud as raw material by operating a pilot plant having a treating capacity of 100 m<sup>3</sup>/hr. of feeding gas. On basis of the results obtained the properties of the yellow mud catalyst are compared with these those of other catalysts as summarized in the following Table. (See page 6A)

### Simplified Coal or Peat Low Temperature Carbonization Furnace Suitable to Manipulate in Coal Mines.

An internally heated, rectangularly shaped brick furnace having a charging capacity of 300 kg coal per one operation has been experimentally built and examined, the carbonization product being drawn out from the bottom of the furnace. The conclusion led was that this furnace requiring a small amount of steel bar is easily constructed and the coal is suitably treated by the coal miners for the purpose of low temp carbonization.

On basis of the results of investigation the commercial enlargement of the furnace of this type was under examination.

The conclusion is outlined as follows.

1. Irrespective of the classification of coal, powdered or block coal, bituminous or nonbituminous coal is equally used for the charge of the furnace.



2. The furnace is easily constructed and handy for operation.
  3. The Low temp. tar is obtainable
  4. The duration of carbonization is 10 - 15 hrs. for the 300kg. charging experimental furnace.
- The result of the carbonization experiment is exemplified as follows:

Charging Coal	Yield of Tar in %
Ubari Coal	10 - 12
Minami-nayosi Coal	10 - 14
Toban-Takahagi Coal	6
Takasaki Peat	3.5

Catalyst			Feed Gas		Yield of Oil cc/m <sup>3</sup>	Reaction Temp. °C	Life of Catalyser Months	NOTE
Kind		Composition	Comp. CO:H <sub>2</sub>	Space Velocity				
Iron Catalyst	With Boric Acid	Fe 100	1:2	About 100	86	230	3	Large Quantity of HNO <sub>3</sub> Required for fabricating Catalyser
		Cu 25				-		
		Mn 2				250		
		H <sub>2</sub> BO <sub>3</sub> 20						
		K <sub>2</sub> CO <sub>3</sub> 20						
		Kieselguhr 125						
	Without Boric Acid	Fe 100	"	"	60	"	1	
		Cu 25						
		K <sub>2</sub> CO <sub>3</sub> 6						
		Kieselguhr 125						
Yellow Mud Catalyser		Yellow Mud 100	"	"	73	"	2	HNO <sub>3</sub> , Cu, Mn, etc. required are small
		Cu 0.5						
		Mn 0.5						
		K <sub>2</sub> CO <sub>3</sub> 4.0						
Nickel Catalyser		Co 100	"	"	95	180	6	
		Cu 25						
		Mg 8						
		K CO 7						
		Kieselguhr 200						
					100	200		

## Volatile Liquid Fuel From Low Temperature Tar

### 1. Catalytic Cracking of Middle Oil Fraction of Low Temperature Tar

Catalyst	Active Carbon	Kanuma-Earth	Active Yellow Mud.
Reaction Temp °C	450	500	400
Space Velocity	1.0	1.0	0.5
200 °C Fraction, Yield in %	25	25	40
Acidic Compound in Fabricated Gasoline in %	15 - 20	20 - 25	20
Remarks	Acidic oil compounds in the charge middle oil fraction Amount to 40%		

### 2. Vapor Phase Refining of straight Run and Cracked Gasoline Fraction.

Catalyst	Active Clay	Kanuma-Earth	Active Yellow Mud.
Reaction Temp °C	350	350 - 400	350 - 400
Space Velocity	below 0.5	below 0.5	below 0.5

The yield of gasoline obtained was about 60 - 70%, the amount of acidic oil being less than 10%. The coloration was not eminent and the stability was prominently increased but detailed examination was stopped.

3. The charging tar containing 40 - 50% of acidic oil, added with 15 - 20% of calcium hydroxide and left standing about 2 days, was distilled. The yield of distillate was 60 - 70% against the charged tar, the acidic oil compounds being decreased to 15 - 20%. When left standing for only a short time after addition of calcium hydroxide the decrease in acidic oil component was not observed.

Kanuma earth active clay, yellow mud, etc. have no effect as calcium hydroxide.

## Manufacture of Aviation Gasoline From Camphor And Camphor Oil

1. **Aviation Gasoline from Camphor.**  
Camphor dissolved in a light oil for instance in the Fischers absorption oil and vaporised is passed thro the phosphoric acid-kieselguhr catalyst at 250 - 350°C with the space velocity 0.3 0.35 (as sol<sup>n</sup>), gives a dehydrated liquid fuel in an yield of 70-80 wt.% against Camphor.
2. **Aviation Gasoline From Camphor oil.**  
Commercial camphor oil contg. ca. 50% of camphor is passed thro the reaction tower packed with active clay at 350-400°C with the space velocity 0.1-0.2. The aviation gasoline thus obtained in an yield of 50-60% is available for the alcohol mixed fuel. This gasoline contains, however, somehow a large amount of gum and is of slightly acidic character.

The heavy fraction may be used for the heavy oil or for the raw material of lub. oil. The life of clay catalyst is shortly limited.

### Utilization Of Pine Root Oil

The fabrication of aviation gasoline from the pine root oil has been studied and the several processes have been developed, the executive conditions also being determined.

The studies on the treatment of the pine root oil began at the end of 1943, and in the first period the utilization of installations found in the existing petroleum refinery plants was aimed, whilst in the last period of the war these existing installations have gradually destroyed by the air raids and could no more be reliable. Therefore the importance was attached to the simplified fabrication in a small scale, such as simplified contact reforming in this period.

1. **Contact Distillation.**  
The pine root oil mixed with active clay, stirred, heated was submitted to the distillation and the distillate was rectified to obtain the aviation gasoline (cf Flow sheet I).

Properties of Aviation Gasoline thus obtained:

Sp.Gr.	0.850
Dist. Range	70°C
1. B	160"
50%	206"
97%	210"
Dry Pt.	80
Octane Value	84
with 0.15% vol.	10
leading	7mg/100 c.c.
Acid value	
Gum Content	
Oxidation Induction Period	5 hrs.

2. Catalytic Reforming.

The pine root oil depitched was distilled and the distillate was charged into the distillation kettle to the vapor outlet of distillation kettle the reaction column packed with the active clay are directly attached. The catalytic reformat thus obtained was rectified to catch the aviation gasoline (cf Flow sheet II).

Properties of Aviation Gasoline thus obtained:

Sp. Gr.	0845
Dist. Range	80°C
I. B.	170 "
50%	202 "
97%	220 "
Dry Pt.	83
Octane Value	87
on 05% vol. leading	5 mg./100 c.c.
Gum Content	4 hr.
Oxidation Induction Period	1.5
Acid value.	

3. Catalytic Cracking.

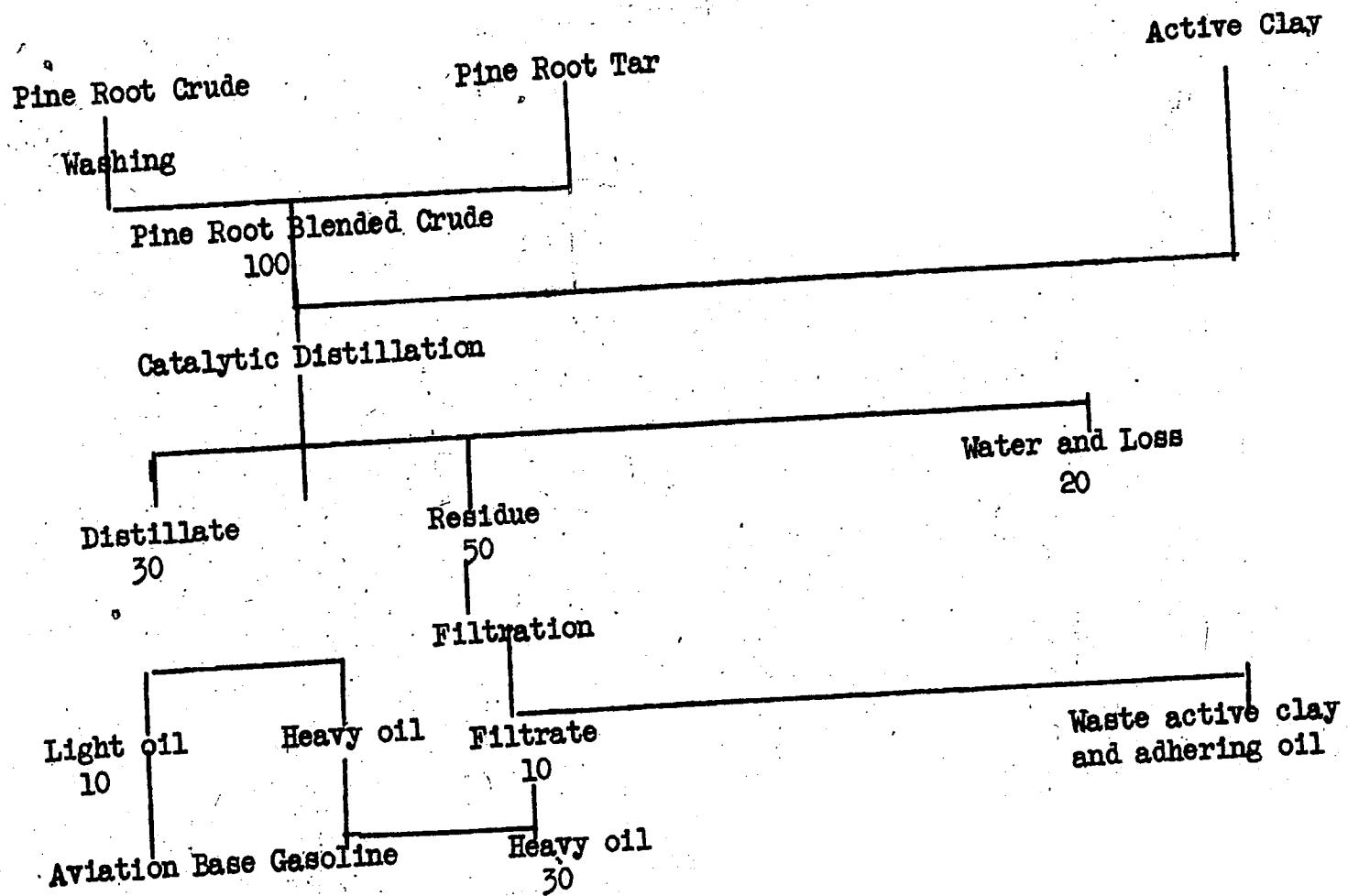
When catalytically cracking the single pine root oil the catalyst was heavily dirtied and its regeneration was very difficult. Therefore the suitable petroleum fraction was blended before the pine root oil was submitted to the catalytic cracking. This process has however never been carried out in a large scale.

4. Hydroreforming.

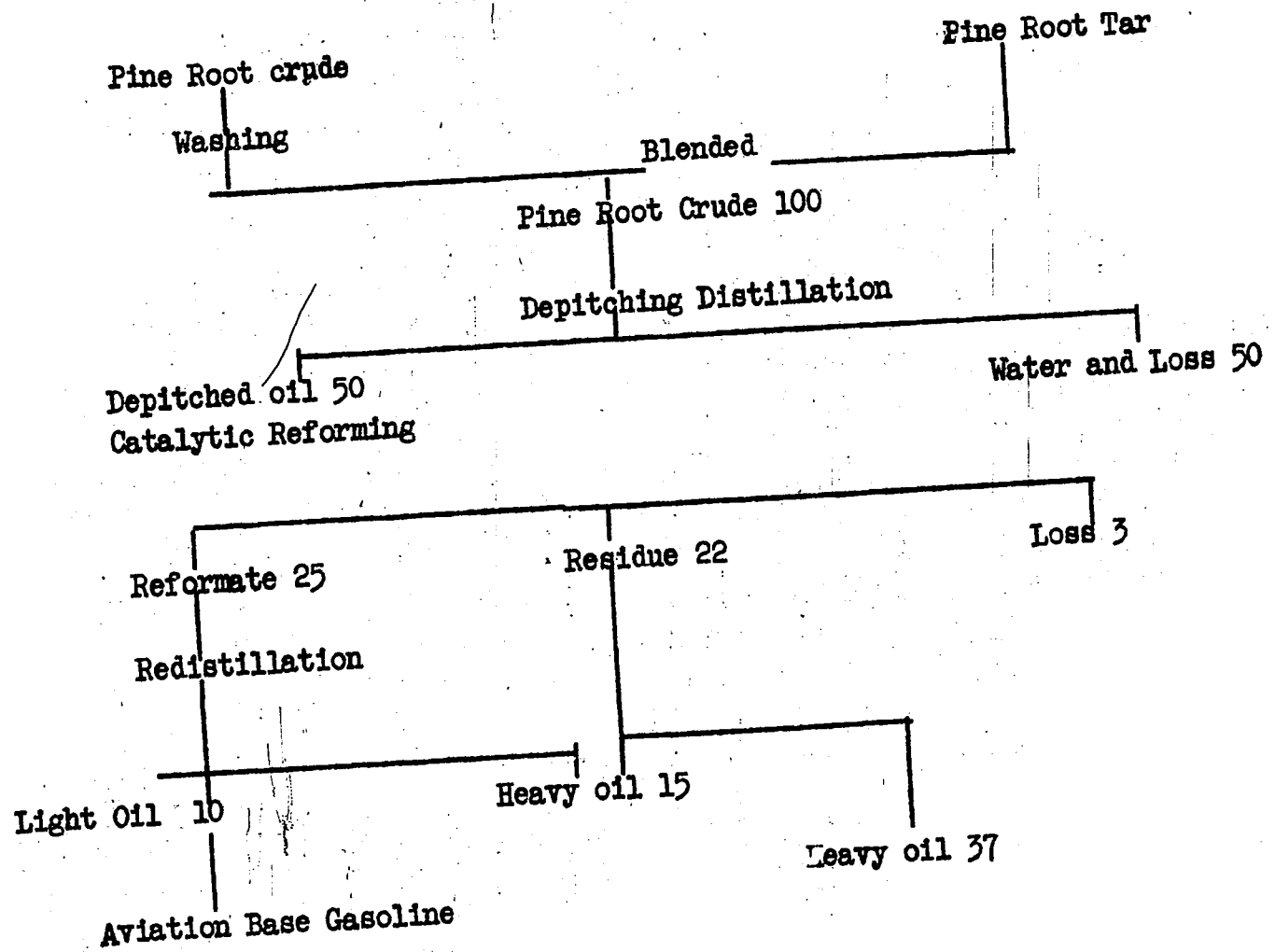
The light fraction of pine root oil topped was stabilized by the hydrogenation in presence of the nickel catalyst.

5. Hydrocracking.

FLOW SHEET 1.



FLOW SHEET II



High Pressure Hydrocracking of Pine  
Root Oil Fraction

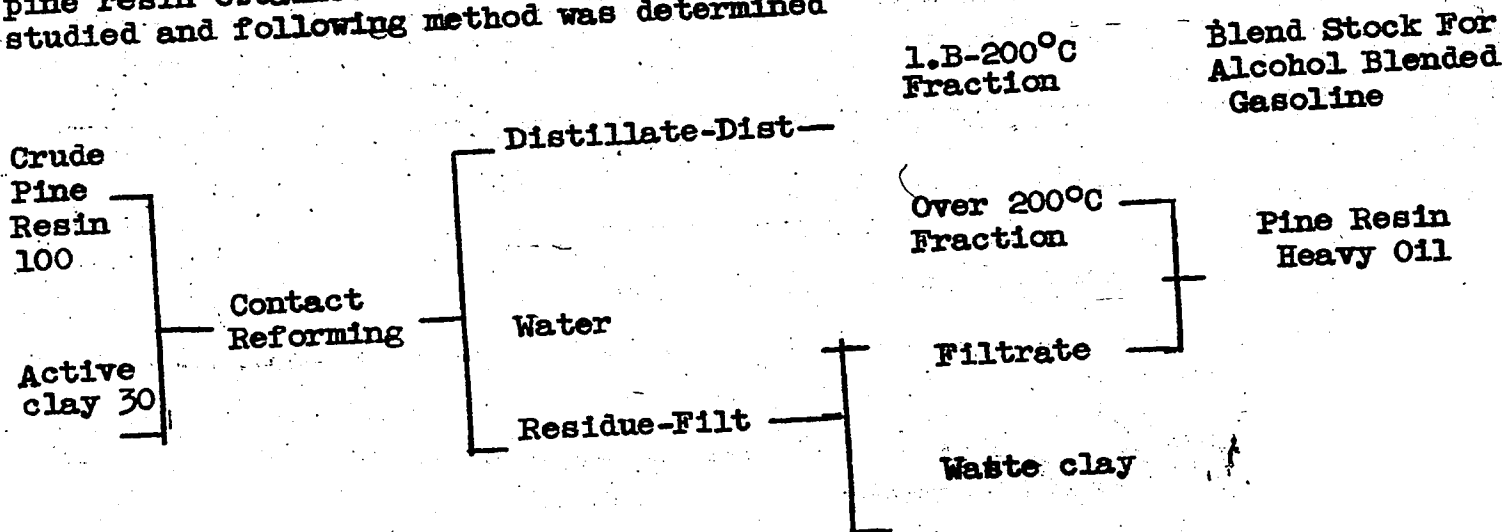
The 95 octane Aviation gasoline has been obtained in an yield ca 50% by the hydrocracking of the light oil fraction of pine root oil, the life of catalyst being considered to be at least over  $\frac{1}{2}$

The results of experiment are summarized as follows:

Catalyst	Molybdenum trisulfide
Oil velocity	1000 c.c./hr.
H <sub>2</sub> velocity	1000 L/hr.
Liquid space velocity	$\frac{1}{1}$
Yield of Aviation Gasoline	50 - 60%
Octane value	on 0.15 vol % leading 94 --95

Simplified Treating Method for Crude Pine Resin

Simplified method of manufacturing the aviation gasoline from the pine resin obtained from the pine tree by cutting its bark has been studied and following method was determined



General Properties of the finished Products

1. General Properties of Pine Resin Gasoline

appearance	colorless, clear
Sp. Gr. D15/4°C	0.82 - 0.83
Acid value	0.2 - 0.4
Reid Vap Press Kg/cm <sub>2</sub> at 40°C	0.1
Solidification Temp Engler Distillation over Pt.	below - 50°C
10%	60°C
50%	130°C
90%	170°C
Octane Value	195°C
Gum Content mg/100c.c.	3.75 - 4
Oxidation Induction Period	90 - 120 mins

2. General Properties of Pine Resin Heavy Oil

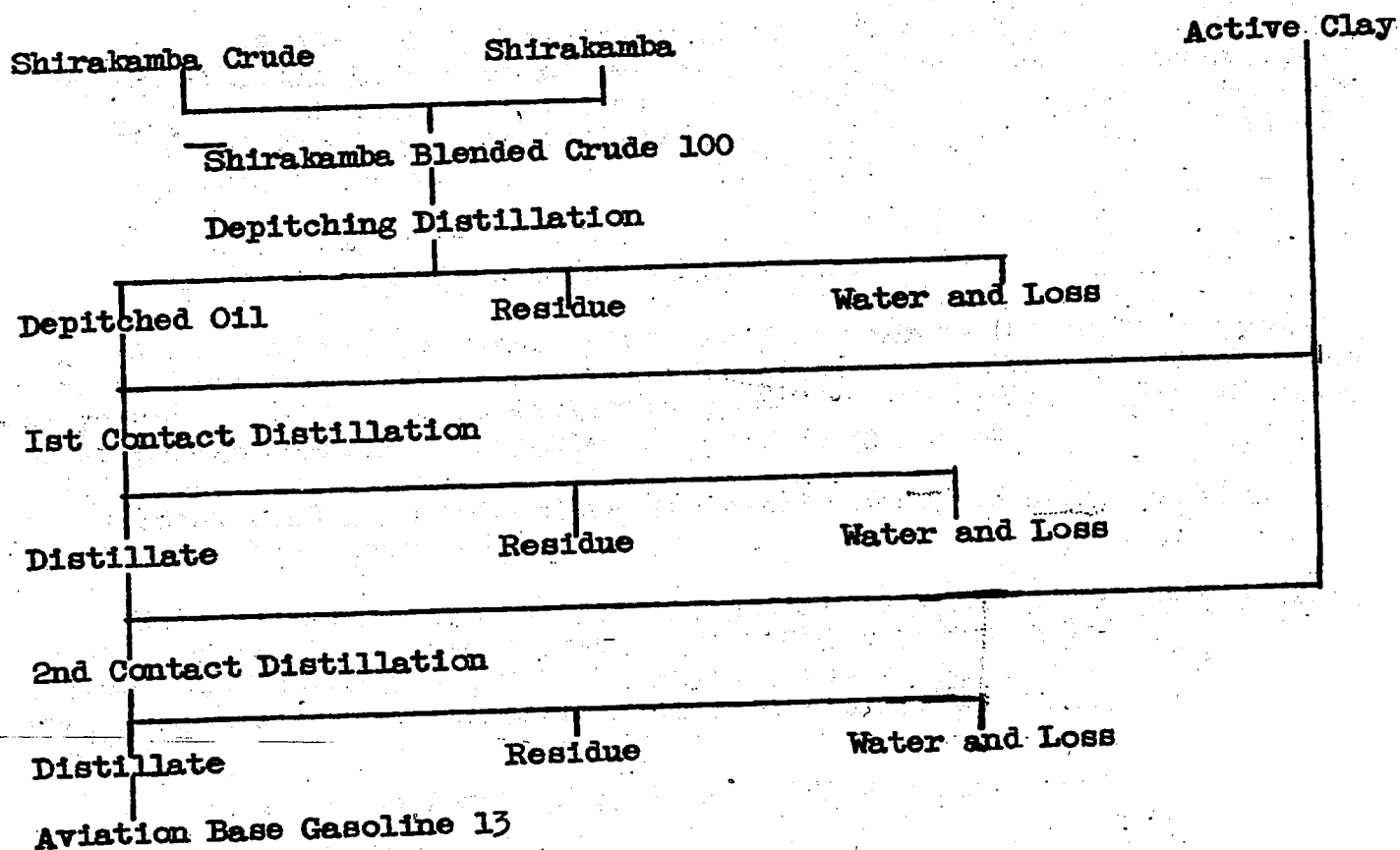
appearance	Yellowish Green
Sp. Gr. D15/4°C	Dark
Acid value	0.91 - 0.94
solidification temp.	0.0 - 0.3
Flash Pt	below - 15°C
Viscosity (Redwood) at 30°C	100 - 110°C
	50 - 60



## Treatment of Shirakamba Bark Oil

The dry distillation of outerbark of shirakamba tree gives 50% of dry distillate. In the southern district of Honshu and Hokkaido where shirakamba trees are abundantly found, this bark oil also is considered to be a valuable source for liquid fuel. The treatment for obtaining the aviation gasoline is carried out almost same as that for the pine root oil. The Yield of aviation gasoline is however a little higher than that from the pine root oil.

The properties of aviation gasoline obtained are nearly equal to those from the pine root oil but it contains a little more lower boiling fraction than the pine root aviation gasoline.



### Manufacture of Aviation Gasoline from Orange Peel

Essential oil rich in limonene obtained from the crude orange peel by pressing with the roller or by the steam distillation of the dried peel is catalytically reformed in presence of the Active clay catalyst to the aviation gasoline.

The practical application of this method was under examination but was stopped owing to the sudden change in the natural situation.

## Manufacture of Aviation Gasoline By the Treatment Of Needle Leaves

The essential oil obtained by the steam distillation on needle leaves such as pine or cedar leaves is catalytically reformed in presence of active clay catalyst

The large scale practice of the process under examination was stopped on account of the sudden change of natural situation.

## Manufacture of Etherified Alcohol

When 94% Alcohol is passed at 210°C through the active clay catalyst with the Liquid space velocity 0.5-2, the liquid product containing 50-70% of ether is obtained in a liquid yield of over 95%. The etherified alcohol thus obtained is available for the aviation fuel of good starting property.

## Dehydration of Ethyl Alcohol

Absolute Ethyl Alcohol is required for manufacturing the gasoline alcohol mixed fuel, whereas for the manufacture of absolute alcohol the dehydrating agent such as dichlorethylene, benzin-benzol mixture which is at present hardly obtainable in Japan is required.

Considered from this situation easily obtainable dehydrating agents have been searched for.

With active Alumina 94-95% alcohol is dehydrated to the 99% (each by wt %) at first, when dehydrated at 80-100°C with space velocity 0.2-0.3 but the studies on the life of catalyst, the variation in dehydrating rate etc. remain still unfinished. Fullers earth and silica gel give no good result.

## Addition Agents for the Alcohol Gasoline Blend

1. Separation Protecting Agent.  
Laurylamine, the most powerful separation protecting agent for the alcohol gasoline blend, has some difficulties in the its next effective and has practicability.
2. Anticorrosive Agent.  
As the anticorrosive agent for the alcohol gasoline blend for aluminium alloys the sodium salt of naphth Henec acid obtained from the waste soda soil resulting from refining of the natural petroleum product to obtain the lubricating oil has been evidenced the most effective. The amount to be added to such a blend is about 0.2%.

## LUBRICANT MANUFACTURE

### Manufacture of Aerolub Oil from Saponifiable Oil

The original method characterized by producing monoolefine with the ZnO - ZnCl<sub>2</sub> catalyst involved a disadvantage of giving during the hydrogenation a great amount of solid product through the mutual action of catalyst material, which stops the reaction tubes and others and disturbs the smooth running. The investigation has therefore been carried out to remove this obstacle and the following method was drafted.

The fatty acid obtained by the saponification of hardened fatty oil and added with the mixed catalyst consisting of 2% of iron powder (yellow earth), 3% of ZnCl<sub>2</sub> and 0.06% of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and thrown into reaction at 350°C for 2 hr. under about over 50 atoms of hydrogen press., gives in an yield of about 60% the monoolefine rich fraction (the yield of monoolefine is somewhat lowered as compared with the case where the ZnO-ZnCl<sub>2</sub> catalyst is used.)

This monoolefine fraction added with 20% of naphthalene and 20% of dehydrated acid clay and thrown into reaction at 200°C for 5 hrs. gives an orange yellow phosphorescent oil. When acid clay and non reacted naphthalene removed, the aerolub oil is obtained in a yield of 25% against the raw material fatty acid.

The yield of Luboil is somewhat elevated when Alchloride instead of acid clay is used for the catalyst for polymerisation.

### Catalyst for Production of Aerolub Oil By Polymerisation and Hydrogenation of Soja-Bean Oil

Original Method - the soja bean oil polymerised at 320°C for 8 hrs. with the Active clay catalyst was submitted to the 2 step-Hydrogenation i.e. first to that with Molybdenum trisulfide and secondly to that with Ni catalyst to the Aerolub oil.

This method has now been studied in view of further improving to simplify it and succeeded in the single step complete hydrogenation in the laboratory exp. by using the Ni or Ni-Mo mixed catalyst, the result being verified by the continuous pilot plant operation and the conditions for the large plant operation were determined.

### Manufacture of Aerolub Oil From Soja-Bean Oil

The original method has consisted in the polymerisation of soja bean oil, the hydrocracking of polymerised soja-Bean oil in presence of molybdenum trisulfide catalyst, the hydrogenation of resultant oil with Ni-catalyst and topping in vacuo to obtain the aerolub of the desired viscosity. The method has been investigated in order to further simplify it and to find the substitute free from the deficient raw material of catalyst. The consequent modification can be optomized as follows.

Soja Bean oil thermally polymerised at 330-340°C under reduced press. of 750 m/m for 24 hrs. gives in about a 90% yield a dark brown, highly viscous polymerised oil of Iodine value about 60.

The Hydrogenation of this oil in presence of about 60% Cu catalyst (Cu:Ni:Acid Clay = 1:1:1) under 150 atm. of hydrogen press. at 350°C for 3 hrs. gives a hydrocarbon of bluish purple color the vacum distillation of the resulting oil with about 20% of Acid clay added yields an aerolub of the desired viscosity.

**Pilot Plant Research on the Manufacture of Aerooil  
From Polymerised Soja-Bean Oil By Hydrogenation**

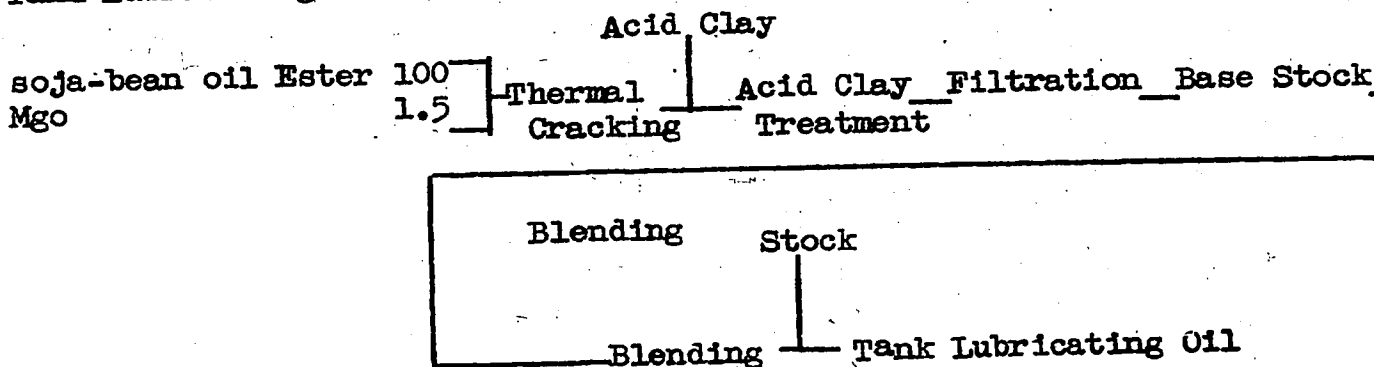
In Connection with the manufacturing method of Aerooil from polymerised Soja-bean oil by its hydrogenation in presence of the Cu system catalyst, the conditions for the industrial operation have been studied through the continuous hydrogenation in the pilot plant with the following results.

1. System Liquid Phase Hydrocracking with the flowing Catalyst
2. Reaction Conditions Press. 150 kg/cm<sup>2</sup> Temp. 320 - 360°C  
Oil Velocity 1/4 vol per hr. per vol of Reaction Tube  
Hydrogen Velocity 2000 Vol. per hr. per Vol of Reaction Tube
3. Catalyst Cu - Ni - Acid Clay system 3 - 5% as metallic Oxide

**Manufacture of High Grade Motor Oil from Saponifiable Oil**

1. High Grade motor oil  
Fatty oil 90  
Cracked oil 10  
Mgo 12  
Active Clay  
Thermal Cracking → Active clay Treatment → Filtration → Finished Product  
Yield Against base fatty oil 50 - 55%

2. Superheated steam cylinder oil  
The high grade motor oil obtained by the forgoing process, distilled in vacuo and topped gives the superheated steam cylinder oil, the yield of oil being 40% against the base fatty oil.
3. Tank Lubricating Oil



## Utilization of Rubber As A Source of Lubricating Oil

1. The examination of a liquid product obtained by the following process and seemingly available as the lubricating oil has proven its inferiority in properties, especially in stability. The practicability of this lubricating oil was thus rendered quite helpless so that the further examination was stopped.
  - (1) Crude rubber is liquified by the thermal depolymerization
  - (2) The light oil fraction is stripped by the vacuum distillation
  - (3) The foregoing fraction is polymerised with the acid clay catalyst, the yield amounting to 40% against charged crude rubber.
  
2. An automobile lubricating oil fabricated by the thermal depolymerization of crude rubber dissolved in petroleum light oil fraction in presence of the acid clay or aluminum chloride catalyst, filtration, topping, followed with blending of the resultant viscous liquid to such a light lubricating oil as machine oil, answers almost to the requirements of the specification, whilst various troubles occur in practice.

The improvement has been therefore undertaken to remove these obstacles. It was proven that about 20% addition of the synthetic lubricating oil obtained from fatty oil is most effective for the present purpose.

### Addition Materials to Lubricating Oil

1. **Antioxidant**  
 The org phosphides such as tributylphosphides, tricresylphosphides act in general singly as the antioxidant of moderate strength for the lub. oil. Of the vulcanisation accelerators the reduce substances, for example, dibenzodithiazoldisulfide further increase the effect which is irrespective of the manufacturing process of the base oil, soja Bean lipid having the same effect as the foregoing phosphides.

The antioxidative effect is especially remarkable on the synthetic mineral oils, being tolerable for castor oil. As obvious from the following example the amount of Antioxidant added to the oil lies in general in and order of 0.01%.

Tributyl phosphide	0.2%	against base oil
Dibenzodithiazlphosphide	0.05%	"
Soja bean lipid	0.2%	"
Dibenzodithiazlphosphide	0.05%	"

2. **Oiliness Improver**  
 The allyl alkylketons are effective as the oiliness improver. Stearophenone added in an amount of about 0.1% to the mineral oil results in an marked improvement of oiliness, stearophenone the molecule of which contains toluol instead of benzol being highly effective for the present purpose.

## CHEMICAL ENGINEERING

### Construction of the Catalytic Reaction Apparatus

As the fundamental examination the distribution of Temperature and air stream in a layer packed with the catalyst has been determined.

It was proved the temperature gradient in the radial direction in the tubular packed layer is parabolic, the mathematical analysis also being undertaken.

As an application, the reaction velocity of butanol dehydration for fabricating isooctane from butanol was studied and this reaction was studied and this reaction was proved a primary reaction. On basis of this, a steel plate reaction apparatus was proposed against the multitubular one formerly used. In this reaction tower a number of steel box for packing the catalyst are superposed inside the brick furnace and the reacting Gas passes successively these boxes, the temperature being regulated by circulating the hot air. The breadth of the box is selected in the arange of 5 - 15 cm in accordance with the magnitude of reaction heat, construction of the reaction tower being convenient. A semi-commercial experiment with this reaction tower for dehydration of butanol gave a yield of 94% butylene.

### Oil Cooling Synthetic Petroleum Furnace

For converting the hot water cooling synthetic petroleum furnace for the cobalt catalyst into the furnace for iron catalyst there occurs a difficult problem that the pressure of hot water reaction temperature of iron catalyst and the strength of the furnace can no more tolerate this high pressure. To avoid this difficulty the use of proper oil boiling at about 200°C instead of hot water was considered for facilitating this conversion. Accordingly, the heat transmission in oil cooling system and the selection of oil have been studied from the standpoint of chemical engineering and was in the stage of going into practice.

### Studies on the Heating Furnace

The engineering analysis of the furnace of equiflux type was undertaken along with the measurement of the relationship between flame length and quantity of primary air as well as the temperature distribution in flame.

Results obtained were that the length of flame in the industrial furnace is about 60 times of the diameter of burner and is shortened by 20% by mixing the primary air.

## Heat Exchanger Having No Steel Tubes (Made with Steel Plates)

For the purpose of economizing the steel tube, a heat exchanger made with steel plates of floating head type was developed and a trial heat exchanger having the area of  $5n^2$  has been examined for its heat transmission. It was evidenced that it is same as the heat transmissibility in a tube whose radius is equal to the distance between two plates.

### Flowing Low Temperature Carbonization

This process is a low temperature carbonization using finely powdered coal. The principle of the method consists in grinding finely powdered coal to the particles under 50 meshes, letting it flow through the tube with superheated steam or with hot gas and carrying out the dry carbonization by eventually heating the tube. An examination was started with an equipment having the capacity of treating 10 kg. per hr. It was proved that in this case the tube is apt to be clogged and the good results are hardly obtainable.

Thus this process did not come to completion. As a modification a dry carbonization furnace shaped like a cyclone was constructed and the fundamental experiment was made herewith.

### Measuring Apparatus for Oil Refining

1. Flowmeters and level controllers fabricated by various makers were examined for accuracy along with the function test of the air acting valves. The latter was, however, stopped halfway.
2. In order to measure the thickness of high pressure steel pipe in a convenient way from the outside of the pipe and to avoid the danger ascribable to the uneven thickness a trial thickness meter was fabricated. The principle of this meter consists like as that of the electromagnetic crack finder in utilizing the variation in the electroinductivity of the electromagnetic coil.

### Simplified Heat Resistive Coating

Since a special heating furnace was used for the heat resistive calorizing the simplification for this process was undertaken and succeeded in a method consisting in spreading a spreading agent over the surface of steel pipe and glazing it at  $700^{\circ}\text{C}$  by the gas flame etc. in air. The Heat resistivity is somewhat inferior to that of calorizing but is effective to prolongate the life of heating pipe. An example of the composition of the spreading agent is given below.

Magnesia	35%
Titanium oxide	5%
Aluminium	40%
Alumina	5%
Zinc oxide	10%
Carbon	5%

## Welding of Special Steel

Welding method for chromium-molybdenum steel pipe for high temperature and pressure has been studied and it was ascertained that when preheating at 300-500°C and annealing at 700-750°C the welding is accurately executable. On basis of the experimental results a welding specification of elongation over 15%, tensile strength over 50 kg/cm<sup>2</sup> and Charpy impulsive force over 8 kg/cm<sup>2</sup> was proposed.

## Studies on the Packing Stuff (Substitute for Long Fibred Asbestos)

Packings obtained from the domestic products and substatable for long-fibred asbestos have been examined and the use of those of wirenet reinforced short fibred asbestos, of aluminium foil, of synthetic rubber and etc. has been determined.

## Non-Burned Brick

For fabricating the brick, the crude brick formed must be burned in the heating furnace and plenty of fuel is thus consumed, Non-burned brick fabricated by mixing the proper amount of binder such as calcium oxide and water glass etc. with the cinder already submitted to the thermal action, and subjecting it to natural drying has strength and heat resistance sufficient enough to be used for constructing the furnace of small scale.

## Studies On the Substitute Container

Of the various substitute containers examined no recommendable container is found for liquid fuel excepting those covered with the polyvinyl alcohol varnish.



# UTILIZATION OF FERMENTATION PRODUCTS

## Utilization of Fermentation Products

The fermentation products which from the standpoint of aviation fuel, became the objects of investigation were as follows.

1. Ethyl Alcohol
2. Butyl Alcohol
3. Aceton
4. Butylic Acid
5. Isopropyl Alcohol

In the first period of the war the butanol fermentation was studied as the raw material for synthesizing isooctane.

The commercial production of butyron from Butylic acid was also undertaken; the process has, however, never been executed. In the later period of the war, the general shortage of fuel was anticipated, therefore the lines of work directed to the direct utilization of ethyl alcohol. In these studies the first importance was attached to the problems of main and by raw materials then those of various fermentation processes to elevate the yield, as well as to the problems concerning the plant installations. In the last period of the war the simplification of fabricating equipments and its diminuation have been undertaken in order to take measures to meet the intensification of air-raid.

### Butylic Acid Fermentation

Butylic acid obtained from cane sugar by the butylic acid fermentation was added with calcium carbonate to give calcium butylate from which butyron was fabricated by the dry distillation. In this process the problems to be solved concerned with the isolation of excellent butylic acid bacteria, the amount of by-stuff and calcium carbonate to be added as well as the operation of commercial plant.

These problems were once solved but the practical production has not been executed.

### Selection of Bacterium For Aceton Butanol Fermentation

About 27 kinds of bacteria were collected and the fermentation period, the yield and etc. were compared under varying conditions for treatment, Ph and others using the corn as raw material.

It was evidenced that almost no marked difference is found among these bacterium, but five kinds of them give the excellent fermentation and are comparably universally compatible with the various varying conditions. The yield is below 22% on sugar basis, the fermentation time being 2-3 days.

## Prevention of the Sleeping Phenomenon In Aceton Butanol Fermentation

For the purpose of getting a clear insight into reasons for such phenomena as lowering in yield and prolongation of the time of beginning of fermentation often observed in the aceton butanol fermentation on account of the prolongation of this time or of the dull progress from the beginning of fermentation to the state of main fermentation and etc., kind of microorganism, nutrition, contamination, kind of raw material, treating conditions and other cultivating conditions have been examined without coming to the decided conclusion. As the consequence of further examination undertaken on demolition of the equipment, washing, sterilization and others, it was evidenced the foregoing phenomenon is ascribable to the fact that when cooling the fermentation tank containing the cooked mash after it being transported the contamination found in air enter into this tank with air by dint of the reduced pressure prevailing in the Tank. Consequently, this problem was conveniently solved only by setting an air compressor. Furthermore as the contamination responsible for the sleeping phenomenon 4-5 kinds of bacillus such as several species of lactobacillus, bacillus subtilis and etc. were isolated and the sleeping phenomenon artificially provoked.

## Nitrogen Source for Aceton Butanol Fermentation

In the aceton butanol fermentation using cane sugar as raw material 10% of soja bean residium is used against sugar. Studies have been done to economize this soja bean residium and to find some other substitute nitrogen sources, the results obtained being summarized up as follows.

1. The bacteria can be multiplied only with soja bean residium can be performed by inoculation of this mesh. Then the amount of soja bean residium formerly used can be exonomized by 10%.
2. Regarding other Nitrogen source, such as residua of castor bean, chrysalis peanut and cotton seed, rice-bran, the conditions for pretreatment are nearly equal to those for soja bean residium, i.e. the treatment under pressure of 30 lbs for 30 mins, and the addition of 5-15 on basis of sugar are sufficient enough to the fermentation.

## Alcoholic Fermentation with Cane Sugar As The Primary Raw Material and Soja-bean Residium as the Secondary

For the change from the butanol fermentation to the alcoholic the conditions for the fermentation attaching cane sugar and soja bean residium have been determined.

Soja-bean residium preheated under pressure of 30lbs for 30 mins. is mixed with cane sugar, added with a small amount of ammonium sulfate and calcium oxide and then submitted to the fermentation. The passable results are obtained when adding on basis of sugar 7-10% of soja-bean residium, 0.4 - 0.7% of ammonium sulfate and a little amount of calcium oxide.

#### Substitute Nitrogen Source for Alcoholic Fermentation

With the shortage of soja-bean residium the substitute Nitrogen source was searched and examined for use. It was verified that the residua of castor bean and peanut, rice-bran, powder of arum root and etc. are available for this purpose. On addition of the materials in an amount of 5-10% is sufficient to supply nitrogen required. In addition to the above mentioned a small amount of ammonium sulfate and calcium oxide must be added.

#### Saccharization and Fermentation of Cellulosive Substance

In view of the fact that the fermentation raw materials clash with the provisions, the fabrication of alcohol from fibrous material was considered and the fundamental experiments have been done with various methods such as those of Scholler, Bergius, Jordani etc.

## CATALYST AND MISCELLANEOUS

### Studies on Fabrication Of Catalysts.

1. Catalysts for the Petroleum Catalytic Cracking.  
Activation, Calcination and forming of the natural Fulleris earth have been studied and the data for selecting the apparatus for commercial fabrication and operating process have been obtained. Synthetic catalyst and active clay synthesized from the natural Fulleris earth have been also investigated.
2. Molybdenum Trisulfide.  
A wooden cylindrical tank handy for fabricating general metallic sulfides and especially for mixing the carrier was first made for the experimental purpose and examined. Next a continuous fabrication was studied in order to further simplify the fabrication and the experiment with a semi-commercial plant installed on basis of the results of laboratory experiment was carried out. In this process the finished product was dried by circulating the heated gas under ordinary pressure instead of being dried in vacuo.
3. Phosphoric Acid Catalyst for Butene Polymerization.  
The fabrication of the solid phosphoric acid catalyst was studied. In view of the deficiency of domestic phosphoric acid source, the catalyst containing a decreased amount of phosphoric acid and the substitutes containing the natural Fullers earth but not phosphoric acid were also studied. It was evidenced that these catalysts are to some extent practicable when phosphoric acid is consumed away.
4. Nickel Catalyst for Low Pressure Hydrogenation.  
The fabrication of Nickel catalyst for the low pressure hydrogenation of such as isooctane, cracked gasoline, polymerized soja bean oil, pine root oil etc, has been studied. Further in view of the deficient domestic nickel source the economy of the nickel has been undertaken. It was proved that the catalyst whose nickel content is lowered from 50% (generally used) to 10% can be used when the carrier and the forming method is specially contrived.
5. Aluminium Chloride  
The fabrication of anhydrous aluminium chloride from the aluminous shale from northern china and the bituminous coal has been fundamentally studied. It was proved that a high temperature of about  $1000^{\circ}\text{C}$  is required to expel the trace of fixed water for the thermal treatment prior to the chlorination, briquetting of coal is not always necessary if the bituminous coal is properly chosen, and aluminium chloride obtained by the present process is, when used for the olefine polymerization in no respect different from that fabricated from metallic aluminium by the customary process.

## Catalyst for Hydroreforming Of Catalytically Cracked Gasoline

Considered from the deficiency in nickel source in Japan, the catalyst substituted for that of nickel system have been studied. The results obtained are summarized as follows.

1. Metals examined for catalyst raw material. Of Fe, Cu, Mn, Zn, Sn, etc. 2 or 3 are converted into hydroxides with KOH and precipitated on active clay or Kieselguhr and formed to the catalyst. The experiments have carried out in the autoclave.
2. The best result was obtained with the Fe-Cu-Kieselguhr system, but as compared with the Ni catalyst, not only highly elevated temp and press. are required but also a large amount of catalyst is necessary. It is considered therefore that this catalyst can not be practically used as far as the present extent of examination is concerned.

### Simplified Fluidification of Waxy Crude Petroleum Oil

In order to facilitate sending-back of such highly waxy crude petroleum as Pendope crude (m.p. 39°C) which is in the solid state at ordinary temperature, the fluidification has been undertaken by mixing it with addition agents like Paraflow and with other diluents.

No addition agent capable of fluidifying such waxy crude with addition of a smaller amount was found. As the diluent lower boiling hydrocarbon was proved most effective, whilst an equiamount of the oil had to be added to the crude for lowering the solidification temp. to 15°C. Therefore the fluidification by dilution was proved impracticable.

Study on the simple dewaxing of such crude oil at the actual place was not undertaken.

### Studies on the Fabrication Of Reference Fuel

The charcoal absorbed oil of Fisher synthetic petroleum is chiefly composed of hydrocarbons of N-paraffine series and a small amount of those of aromatic series, but is almost free from Napthenic hydrocarbons. It contains about 10% of N-heptane and shows an octane reference fuel for determining the octane rating. A fraction containing a larger amount of N-heptane was washed with sulfuric acid to remove aromatic hydrocarbons and then submitted to the repeated rectification to obtain N-heptane. The rectificate thus obtained in the laboratory had physical constants nearly equal to those of pure N-heptane and the knockmeter indication was also almost as that shown by the American

standard reference fuel. For fabricating somewhat a larger amount of such fuel still there lies many problems to be solved but it can be sufficiently used at least as a secondary reference fuel having about zero octane rating.

#### Thermal Expansion Coefficient of Ethyl Fluid

Since the leading of gasoline is carried out on the volume basis, a volume change due to a varying temperature must affect the amount of ethyl fluid and the leaded octane rating in consequence. To examine this effect, the thermal expansion coefficient of ethyl fluid was determined over a temp. range of 0-40°C at every 5 degrees.

It was evidenced that the volume change of ethyl fluid due to the varying temp. brings about a variation of octane rating smaller than 0.5, a nearly negligible order of magnitude for the routine test work, when sampling 300-500 c.c. of gasoline.

#### Determination Of Tetraethyl Lead In Ethyl Fluid

For the purpose of determining tetraethyl lead in the ethyl fluid the lead content was estimated by directly oxidizing the former without dissolving it into gasoline, and examined for accuracy of analysis.

It was evidenced that tetraethyl lead in the ethyl fluid can be estimated, when the former is carefully oxidized directly with  $\text{HNO}_3$  into  $\text{Pb}(\text{NO}_3)_2$ , preventing the evaporation loss, then turned into  $\text{PbSO}_4$  with  $\text{H}_2\text{SO}_4$  and gravimetrically determined, with almost the same accuracy as that obtained when the ethyl fluid is dissolved into gasoline and then analysed for lead in accordance with the similar process.