

# THE SYNTHESIS OF TERTIARY BUTYL ETHYL ETHER AND ITS CHARACTER AS THE BLENDED FUEL

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## Introduction

The admixture of certain materials which have a high octane value in gasoline makes a motor fuel of high anti-knocking characteristics. Tetraethyl lead is the best of these materials, but for various reasons can be used only in limited quantities. To further increase the anti-knocking qualities of the fuel, therefore, other materials must be added.

Of the other materials, isooctane and isopentane are most suitable as blending agents. Aniline would also be suitable, except that aniline is difficult to mix in gasoline and there are many obstacles.

Isopropyl ether has a high octane value, but its low calorific power and difficulties of manufacture make it impractical to use.

Tertiary-butyl ether<sup>(1)</sup>  $(\text{CH}_3)_3\text{C}\cdot\text{O}\cdot\text{C}_2\text{H}_5$  belongs to the same series of isopropyl ether and has following physical qualities:

B.P. 75°C.,      Octane Value 115 (C.F.R.),  
 $D_4^{25}$  0.7407,      Calorific Power 9785.

We thought that the synthesis of ter.-butyl ethyl ether was comparatively easy, and its blending octane value was pretty high when we mixed it in gasoline.

Therefore, we studied the synthesis of ter.-butyl ethyl ether, and at the same time we engaged in this experiment to investigate its faculty as blending agent of motor fuels.

## Synthesis of Tertiary Butyl Ethyl Ether

We studied two methods of the synthesis of ter.-butyl ethyl ether. One is the dehydration of ter.-butyl alcohol and ethyl alcohol, and another is the direct combination of isobutylene and ethyl alcohol.

### I. *Synthesis from ter.-Butyl Alcohol and Ethyl Alcohol*

*Production of ter.-Butyl Alcohol* We put 200 cc. of 60 per cent sulphuric acid in a Lintner pressure bottle, and cooled it below  $-20^\circ\text{C}$ . Then 120 cc. of liquefied isobutylene was mixed with it and 5 gr. of potassium ferrocyanide was added as a catalyst of hydration. The bottle was corked tightly and was shaken for four hours by a shaking machine at the same time cooling with ice-water.

(1) T. W. Evans and K. R. Edlund, *Ind. Eng. Chem.*, 28, 1186 (1936).

After shaking; the cork was taken off to vaporize the unreacted isobutylene, and the liquid was poured into ice-water, then was diluted by three volumes of the distilled water. This liquid was neutralized with sodium carbonate solution, and was dried with anhydrous sodium carbonate.

120 cc. of tertiary butyl alcohol was obtained by the distilling of the liquid at 78°-81°C. (this fraction was a constant-boiling mixture of ter-butyl alcohol and water).

In the above experiment, we found no isooctene which was a polymer of isobutylene. But in the case of using 70 per. cent solution of sulphuric acid or shaking at ordinary temperature, we found isooctene 2-3 per cent.

*Synthesis of ter-Butyl Ethyl Ether* In the following method<sup>(2)</sup> ter-butyl ethyl ether was obtained by the dehydration of ter-butyl alcohol and ethyl alcohol, using sulphuric acid.

We studied the suitability of its process in the next six methods.

1) We put 92 gr. of ethyl alcohol and 300 cc. of 15% sulphuric acid in a Claisen flask and distilled the mixture adding 74 gr. of ter-butyl alcohol by means of a separating funnel which was connected to the upper part of the flask.

2) Same as (1), but using 18% H<sub>2</sub>SO<sub>4</sub>, mixing the 3 liquids together and distilling.

3) We boiled the mixture, alcohol and 15% sulphuric acid solution, in a flask which was connected to a reflux condenser, added ter-butyl alcohol, continued to boil the mixture for half hour, and then distilled it.

4) Same as (3) but using 18% H<sub>2</sub>SO<sub>4</sub>.

5) Same as (1) but boiling for 3 hours often adding the tertiary butyl alcohol.

6) Same as (5) but using 18% H<sub>2</sub>SO<sub>4</sub>.

The yields of tertiary butyl ethyl ether from the six methods are given in table 1 below:

Table 1. The Yields of ter-Butyl Ethyl Ether  
(from ter-butyl alcohol 74 gr. and ethyl alcohol 92 gr.)

In 300 cc. of 15% H <sub>2</sub> SO <sub>4</sub>				In 300 cc. of 18% H <sub>2</sub> SO <sub>4</sub>			
Temp. of Distill. °C.	Vol. of Fraction Method			Temp. of Distill. °C.	Vol. of Fraction Method		
	(1)	(3)	(5)		(2)	(4)	(6)
		cc.				cc.	
48~78	80	90	75	~68	20	12	44
				68~76	22	28	14
78~85	54	32	40	76~79	39	56	42
				79~84	20	30	2~3

From table 1, it will be seen that when the 15 per cent solution of sulphuric acid was used there were few bi-reactions than when using the 18 per cent solution,

(2) J. F. Norris and G. W. Rigby, *loc. cit.*

and when the mixture (ter.-butyl alcohol, ethyl alcohol, and sulphuric acid) was boiled previously, the result was very good.

After crude ter.-butyl ethyl ether was washed by water, it was dried with anhydrous sodium carbonate and distilled.

Almost of all was distilled at 70°-73°C.

## II. Synthesis from Isobutylene and Ethyl Alcohol

If isobutylene gas is bubbled through a warm mixture of ethyl alcohol and sulphuric acid, the isobutylene will combine with the alcohol to form ter.-butyl ethyl ether. Liquefied isobutylene obtained by catalytic dehydration of isobutyl alcohol (using acid clay and alumina) was used in the experiment.

This isobutylene was stored in a cooling receiver (*a*), see figure 1, which was in a Dewar flask containing dry-ice and petroleum. The mixture of ethyl alcohol and

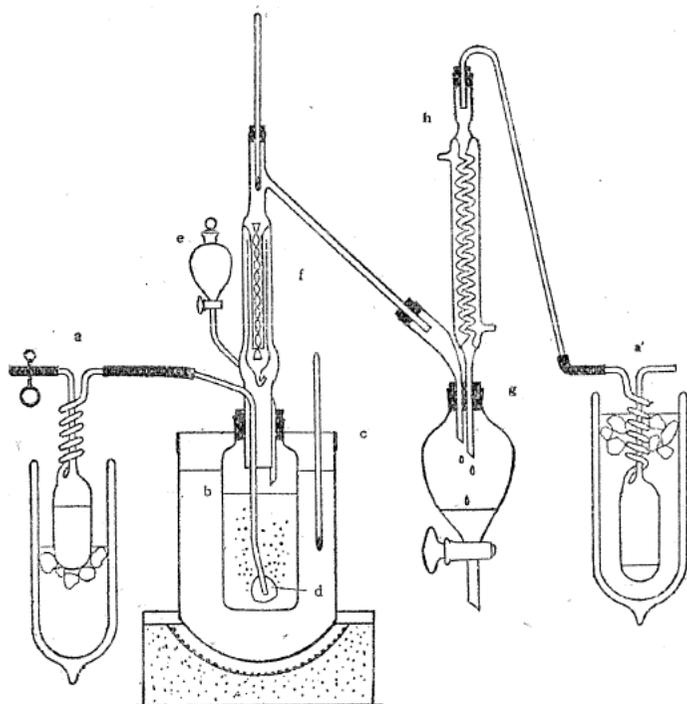


Fig. 1. Apparatus for Production of ter.-Butyl Ethyl Ether (direct method)

and sulphuric acid was warmed at 80°C. in a reaction bottle (*b*), and isobutylene gas introduced. Purity of ethyl alcohol used was 98 per cent. Isobutylene was generated moderately in the cooling receiver, gradually exposing out of the Dewar flask. Thus vapourized isobutylene was led into the reaction bottle and its pass-speed was regulated by observing the bulk of bubbling foam in the reaction bottle.

Isobutylene, bubbling in the bottle, dissolved partly in the mixture of ethyl alcohol and sulphuric acid. This dissolved isobutylene combined with alcohol by the catalytic action of sulphuric acid, and became ter.-butyl ethyl ether. This ter.-butyl ethyl ether was removed from the mixed solution and vapourized into the Widmer refluxer (*f*), accompanied by alcohol and unreacted isobutylene gas.

The temperature at the top of the refluxer was kept at 50 to 60°C., as determined previously during distillation of the ethyl alcohol and tertiary butyl ethyl ether

mixture. Care was taken to keep the unreacted isobutylene gas from blowing off the alcohol.

The size of the foam of isobutylene in the bottle and the height from the nozzle to the surface of the liquid have a very important relation to its reaction. So, the foam was made as fine as possible by means of a glass fiber cap (*d*), (dia. about 2 cm.), surrounding the nozzle (its pipe, dia. 4 mm.). Supplying new alcohol to replace the alcohol blown off by unreacted isobutylene, the height from the cap to the liquid surface was always kept to 10-12 cm.

In the cooling receiver (*a'*), same cooling as (*a*), the unreacted isobutylene gas, which was separated from the condensed liquid in a receiver (*g*) and passed through a spiral condenser (*h*), was recovered. When the pass speed of isobutylene gas was higher in the reaction bottle, the recovered isobutylene in (*a'*) contained ter-butyl ethyl ether, about 5-20 per cent.

In the receiver (*g*), isobutylene also was considerably dissolved in the mixture of ter-butyl ethyl ether and ethyl alcohol. Therefore, the mixture was shaken with the distilled water, in rate of 4 to 1, to drive out most of the dissolved isobutylene. An oily layer was separated from the liquid by this shaking, and this layer was washed over again and dried with anhydrous sodium carbonate.

This layer was ter-butyl ethyl ether. The results of these experiments are shown in table 2 below:

Table 2. Condition of Yields of ter-Butyl Ethyl Ether (direct method)

A	B by vol.	C cc.	D cc.	E cc.	F cc.	G °C.	H °C.	I hour
3	4:1	140	25	150	62	80-85	55-65	5½
4	"	190	45	120	95	75-78	55-67	5
5	"	250	80	195	110	"	"	4½
7	"	220	63	125	82	75-82	-50-	6¾
8	"	200	75	220	80	"	"	5½
10	8:1	220	48	120	75	70-82	-58-	6½
11	"	200	30	68	42	-80-	-40-	"
12	"	180	27	175	110	"	-55-	"
14	"	230	50	175	83	"	-60-	5½
15	"	270	55	180	115	78-80	-55-	5
16	"	250	40	220	108	-80-	-60-	6
17	"	130	72	128	74	"	-65-	4

As shown in table 2, we recovered no unreacted isobutylene.

When we diluted the mother-liquid (alcohol and sulphuric acid) in the bottle until three to one and neutralized it with sodium carbonate, the oil matter was not separated. This showed that so much isooctene was not yielded by polymerisation of isobutylene.

We used continuously the mother-liquid till the end of each process (divided in

two processes) by using sulphuric acid and alcohol in the ratio of 1:4 and 1:8. Near the end of the reaction, the solution became reddish-brown, but such a phenomenon did not much effect.

*i.e.*, figure 2 shows the continuous catalytic power of sulphuric acid.

When we distilled the crude ter.-butyl ethyl ether in a Widmer refluxer, we obtained about 15 per cent of all fraction below 50°C. In this lower fraction, there were isobutylene and diethyl ether, but in very small quantities. The distilled ter.-butyl ethyl ether was again distilled in a Podbeilniak fractionating column and a 71°-73°C. fraction obtained (see figure 3.).

In the above testing, if the blowing off by unreacted isobutylene gas is properly controlled, the separation between ter.-butyl ethyl ether and alcohol will be good and so the production of ter.-butyl ethyl ether.

#### Properties of Tertiary Butyl Ethyl Ether

The tertiary butyl ethyl ether obtained had a camphorous odour and was difficult to dissolve in water. Its physical properties were as follows.

Boiling Point 71°-73°C.,

Density  $D_4^{20}$  0.7417,

Refract. Index  $n_D^{20}$  1.37516,

Vapor Pressure 0.463 kg/cm.

The property of ter.-butyl ethyl ether in a blended fuel was as follows. Mixing ter.-butyl ethyl ether into a base gasoline, we tested the blended octane value and the effect of tetraethyl lead by a C.F.R. engine (this engine was operated under the

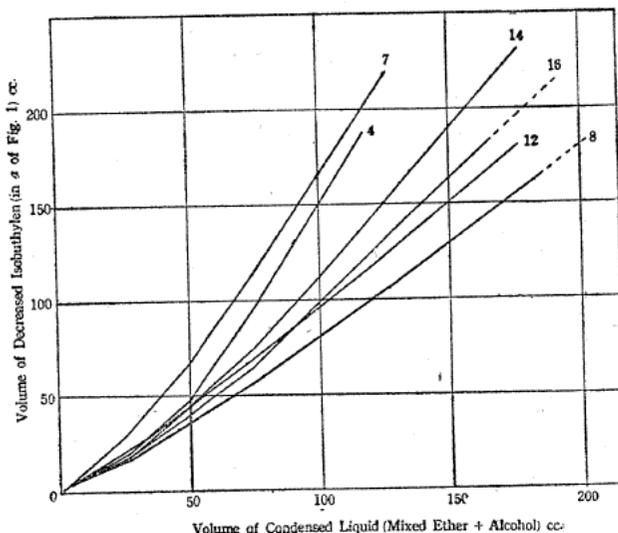


Fig. 2. Reaction Curves of Isobutylene (from Table 2).

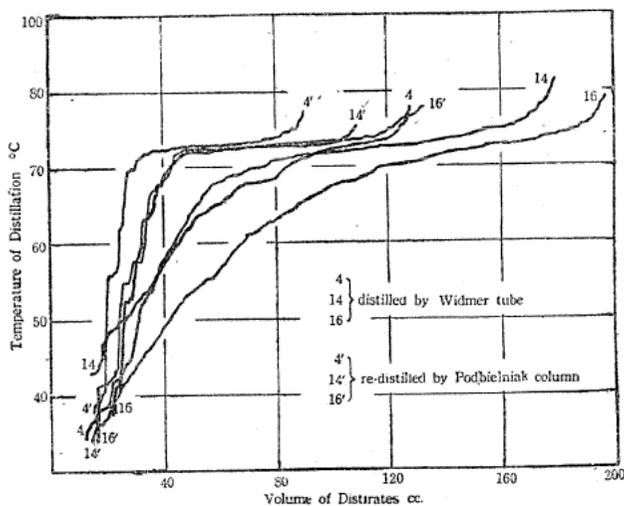


Fig. 3. Distillation of Crude Ether.

standard condition of A.S.T.M.). At the same time, we also tested fuels of isooctane and isopropyl ether, and compared these ability as blending agents. The results are shown in table 3.

Table 3. Blended Octane Value of ter.-Butyl Ethyl Ether, Isooctane, and Isopropyl Ether

	Base <sup>4)</sup> Gasoline	Percentage of Blending			
		10 %	20 %	(25 %) <sup>5)</sup>	30 %
Isooctane <sup>1)</sup>	Single	66.7	69.2	(79.4) <sup>5)</sup>	71.8
	0.1 Lead added	87.5	88.4	(88.8) <sup>6)</sup> (93.2) <sup>5)</sup>	91.0
Isopropyl <sup>2)</sup> Ether	Single	67.3	71.3	—	75.7
	0.1 Lead added	87.4	90.0	—	92.0
ter.-Butyl <sup>3)</sup> Ethyl Ether	Single	69.8	75.5	(83.8) <sup>5)</sup>	80.4
	0.1 Lead added	89.4	92.8	(93.1) <sup>6)</sup>	96.9

- 1) Made by Mitsubishi-Kasei Co.
  - 2) Made by Takeda-Yakuhin Co.
  - 3) We obtained (direct method).
  - 4) Its octane value was 64.2, its blended octane value was 84.8 in case of adding 0.1 % tetraethyl lead.
  - 5) Used base gasoline of 73-octane value, and added 0.085 % lead.
  - 6) In the case of (5), lead was decreased to 0.042 %.
- In 5)-6), we used the ether (from ter.-Bt.-OH and Et.-OH).

The effect of mixing ter.-butyl ethyl ether into the base gasoline was considerably better than that mixing isooctane or isopropyl ether. Moreover, when we added tetraethyl lead in each of these three cases, we also recognized that ter.-butyl ethyl ether had better effect than the other. As in figure 4, the line of ter.-butyl ethyl ether showed us its larger rising than that of isooctane or isopropyl ether. Besides, tetraethyl lead did no harm to the mixed gasoline with ter.-butyl ethyl ether. The effect of 10 per cent addition of ter.-butyl ethyl ether in gasoline nearly equalled the effect of 20 per cent addition of isooctane. When 0.1 per cent of tetraethyl lead had previously been added the effect of 10 per cent addition of ter.-butyl ethyl ether was larger than that of 20 per cent addition of isooctane.

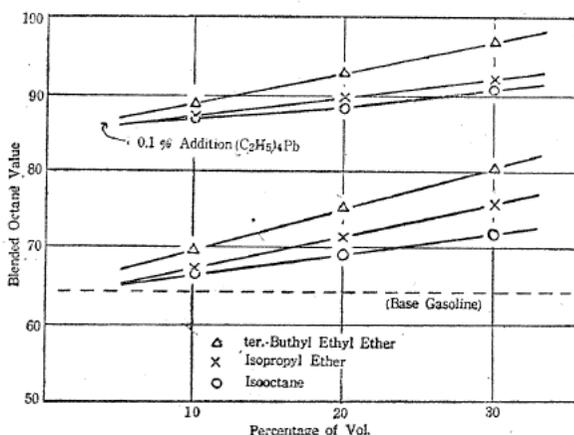


Fig. 4. Comparison of Blended Octane Value

### Summary

1) The synthesis of tertiary butyl ethyl ether by direct combination of isobutylene and alcohol with the catalytic action of sulphuric acid proceeded smoothly.

II) Physical properties of ter.-butyl ethyl ether, boiling point, density, refractive index, and vapor pressure, were figured out. And the blending octane value of it was surveyed by the C.F.R. engine comparing with ones of isooctane, and isopropyl ether.

We recognized that this 'mixed ether,' ter.-butyl ethyl ether, has much higher anti-knocking qualities than the other.

These characteristics are believed to offset the disadvantage of its low colorific power. There is however the danger that some of the tertiary butyl ethyl ether will be changed to peroxide by the action of ultra-violet rays or of the iron surface.

It is, nevertheless, possible to avoid the formation of peroxide and use tertiary butyl ethyl ether and mix it in gasoline with tetra ethyl lead. In this way it is a practical blending agent for motor fuel.