

UNITED STATES PATENT OFFICE

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ALKYLATION PROCESS

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This invention relates to a low temperature alkylation process for producing an alkylate of high anti-knock quality and high flash point.

In order to reduce the hazard from fire which is attendant to the crash landing of aircraft, it has been proposed that the customary flammable gasoline used as fuel be replaced by a material which will not readily ignite at atmospheric temperature, yet will perform satisfactorily in an internal combustion engine of the conventional Otto type. The requirements for such a fuel are that it be substantially equal in anti-knock quality and heating value to conventional high octane number aviation gasolines, yet have a "flash point" high enough so that its vapors will not readily ignite from a spark under atmospheric conditions. A fuel having a Tag closed cup flash point of at least 100° F. may be properly designated as "safety fuel."

We have found that by the proper choice of operating conditions and catalyst the alkylation reaction can be controlled so that when low molecular weight isoparaffins and mono-olefins are alkylated, high octane number isoparaffins boiling in the safety fuel range are produced in relatively high concentration. For example, when isobutane is alkylated with butylenes in the presence of concentrated sulfuric acid in the conventional manner at 35° to 50° F. for the production of alkylate boiling in the gasoline range, that portion of the product which has a volatility suitable for inclusion in safety fuel usually comprises less than 10% (vol.) of the total alkylate, and has an ASTM octane number generally not exceeding 86. We have discovered that when isobutane and butylenes are alkylated, using as a catalyst a mixture of sulfuric acid and ethylene or ethyl sulfate at temperatures below 20° F., an unusually high yield of material boiling above 300° F. and having a flash point above 100° F. is produced. We have also discovered that this material is of superior quality for use as a safety fuel. Thus, when the alkylation temperature was decreased from 38° F. to 0° F., the clear ASTM O. N. of the safety fuel cut increased from 85.2 to 91.1.

In carrying out the alkylation at temperatures below 20° F., it is important to use suitable

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diluents in the sulfuric acid catalyst. The strength of the sulfuric acid used in the low temperature alkylation is about 96% to 98%, preferably about 98%, and such acid will tend to freeze at temperatures between about +20° F. and +30° F. if its freezing point is not suitably depressed. The suitable diluents prevent the sulfuric acid from freezing at temperatures below +20° F. down to as low as -20° F., while they maintain adequate catalytic activity of the acid and effect some regulation of the reaction not fully understood at present.

We have found that ethylene, ethyl sulfate, dimethyl ether, and similar low boiling aliphatic compounds are suitable diluents for the purpose of maintaining the desired catalytic activity in alkylation at the low temperatures. These suitable diluents are characterized by their tendency to exist in the catalyst composition as aliphatic sulfates, being sulfates initially or forming sulfates when absorbed by the acid. They are further characterized as being substances which do not weaken the acid by formation of substantial amounts of water on admixture with the acid. They contain alkyl groups which are lower in molecular weight than the hydrocarbon reactants. For example, they may be compounds which acquire the form of methyl, ethyl, or propyl sulfates in the catalyst for the alkylation of the C₄ isoparaffins with C₄ mono-olefins. Accordingly, the lower alcohols, C₁ to C₃ alkanols, cannot be used except to a very limited extent as diluents, since they have the tendency to form water by reaction with the sulfuric acid.

A minor proportion of diluents is mixed with the sulfuric acid in the catalyst solution, preferably from 0.1 to 0.5 mole per mole of sulfuric acid. By thus limiting the amount of diluent in the catalyst solution, the titratable acidity of the solution can be maintained at a proper concentration above 70%.

The following tabulated data illustrate typical conditions and results of the low temperature alkylation conducted in accordance with the present invention and make a comparison with conventional higher temperature alkylation treatments.

Alkylate safety fuels

Feed Stock.....	Isobutane-Butylenes		
	98% H ₂ SO ₄	98% H ₂ SO ₄	98% H ₂ SO ₄ - Diluent Solution ²
Catalyst.....			
Reactor Temperature °F.....	70	38	0
External Isobutane/Olefin Ratio (mole basis).....	5/1	5/1	5/1
Spent Acid, Percent titratable Acidity.....	87.5	91.2	75
Acid Consumption, lb./gal. of total alkylate, based on degradation 98% to 90% titratable acidity.....	2.2	0.7	(¹)
Aviation Alkylate			
Yield on Total Alkylate, Vol. Percent.....	87.0	87.3	67.6
50% at °F.....	219	220	225
60% at °F.....	235	234	264
F. B. P., °F.....	265	251	348
ASTM O. N., Clear.....	92-93	94.1	93.9
Safety Fuel Cut			
Yield on Total Alkylate, Vol. Percent.....	10	8	23.2
Gravity, °API.....	56.6	55.1	54.4
I. B. P., °F.....	305	314	353
10% at °F.....	323	336	358
50% at °F.....	348	358	362
60% at °F.....	372	384	370
90% at °F.....	401	433	379
F. B. P., °F.....	2	2	2
Bromine Number.....	98	106	120
Tag Flash, °F.....	81.4	85.2	91.1
ASTM O. N., Clear.....			
ASTM O. N. + 3 cc. TEL/gal.....	94.9	98.2	iso + 0.03

¹ Titratable acidity was maintained constant at 75% by the addition of 0.6 lb. fresh catalyst/gallon alkylate. This is equivalent to replacement rate of 0.5 lb. 98% H₂SO₄/gallon alkylate.

² Containing 0.23 mole ethylene/mole H₂SO₄.

Whereas there was comparatively little change in the octane number of the low flash point aviation alkylate, the safety fuel cut increased in clear ASTM octane number from 81.4 to 91.1 as the temperature decreased from 70° F. to 0° F. Furthermore, the yield of safety fuel was considerably higher in the 0° F. operation than it was at higher temperatures (23% vs. 8-10%).

Our invention may be applied in any of the various types of reaction equipment which are generally employed in the petroleum industry for producing aviation alkylate. It is desirable only to provide additional equipment to dissolve the diluents in the acid, such as a vessel in which to absorb ethylene in the fresh sulfuric acid catalyst, additional refrigeration facilities, and a distillation column in which the safety fuel may be fractionated from the other components of the total alkylate product.

It will be noted that of the factors which contribute to production of high anti-knock safety fuel compounds in increased amounts, the most important are the lowering of the temperature and the use of the suitable diluents in the catalyst solution.

The preferred low temperature alkylation reaction temperature is in the proximity of 0° F., e. g., about 0° to 5° F. With the suitable diluents, which in small amounts depress the freezing point of the acid from above +20° F. to below 0° F., the titratable acidity of the catalyst can be maintained at high levels from 70% to about 98%, the alkylate yield and quality being increased with the acidity.

It is of interest to note that low temperature alkylation conditions are favorably used on feeds containing increased proportions of iso-olefins. There are indications that with above 15 volume

per cent of isobutylene in the total olefin feed, there is considerably less catalyst degradation and the quality of the safety fuel cut is substantially improved as compared to a feed in which 15% by volume or less of the olefins is isobutylene. The yield of safety fuel alkylate was shown to be nearly doubled on increasing the volume per cent of isobutylene from 15% to 30% on total olefins in a refinery cut containing 5 to 10% normal butylenes and at least 70% by volume of isobutane.

By using the improved low temperature alkylation conditions, in general, safety fuel alkylates boiling in the range of 300° F. to 420° F. with clear octane numbers above 88 are obtained in yields amounting to about 20 volume per cent of total alkylates; whereas under alkylation conditions conventionally used in the past for producing maximum yields of lower boiling alkylates, only about 10% of material boiling in the range of 300° F. to 420° F. was formed, and this material has clear octane numbers of only 80 to 85.

The improved safety fuel products of this process may be used as an aviation safety fuel base alone, or with other kinds of safety fuel ingredients. They may be used with fuel additives, such as gum inhibitors, dyes, color stabilizers, anti-oxidants, and various anti-knock agents. They are generally to be used with an addition of about 2 to 5 cc. of tetraethyl lead per gallon in formulating a satisfactory aviation fuel.

The invention is not to be limited by the specific examples given for the purpose of illustration but is intended to include modifications which come within the spirit and scope thereof.

We claim:

1. The process of preparing aviation safety fuel components which comprises forming a catalyst solution of sulfuric acid having a strength of about 96% to 98% with a small proportion of an aliphatic sulfate containing alkyl groups of 1 to 3 carbon atoms to depress the freezing point of the acid from above +20° F. to below 0° F., and alkylating a liquefied normally gaseous isoparaffin with a liquefied normally gaseous olefin at a temperature in the range of -20° F. to +20° F. in the presence of said catalyst solution.

2. In an alkylation of isobutane with butylenes, the steps which comprise absorbing into about 98% strength sulfuric acid from 0.1 to 0.5 mole of ethylene per mole of sulfuric acid to form a catalyst solution in which the freezing point of the sulfuric acid is lowered from above +20° F. to below 0° F., alkylating isobutane with butylenes including isobutylene in the presence of said catalyst solution, and maintaining the acidity of said catalyst solution between 70% and 98% while the solution is maintained liquid at a temperature below +20° F.

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