

Topanol A as an Antioxidant for Jet Fuel: Preparation and Application

Ali Mehdizadeh*, Amir Nasser Ahmadi, and Ghasem Khatinzadeh

Chemical Polymeric and Petrochemical Technology Development Research Division, Research Institute of Petroleum Industry, Tehran, Iran

ABSTRACT

Topanol A is a phenolic antioxidant additive, which is used in storage tanks for jet fuels produced in the petroleum refineries throughout the country. Topanol A mostly consists of 2,6-di-t-butylphenol. The conventional methods for the preparation of this compound involve ortho-alkylation of phenol using 2-methylpropene (isobutylene) as the alkylating agent. The compound has been prepared by ortho-alkylation of phenol using 2-methylpropene (isobutylene) as the alkylating agent and aluminum phenolate, prepared in situ using commercial grade aluminum, as the catalyst in bench and pilot plant scales and the synthetic parameters have been optimized. An alternative, cheap alkylating agent, namely Butane-Butene Raffinate (BBR) from Arak Petrochemical Complex, has also been successfully used in the synthesis. Moreover, the product has been characterized by ^1H NMR spectroscopy, and its antioxidant efficiency has been evaluated. Also, the samples prepared have been blended in ATK (Aviation Turbine Kerosene) jet fuel together with another necessary antistatic additive (ASA), and the formulations have been tested by the central quality control laboratory of the National Iranian Oil Refining and Distribution Company (NIORDC). Finally, the results of quality control tests have indicated the efficiency of the prepared formulations with respect to the corresponding specifications and their comparability with authentic additive samples.

Keywords: Topanol A, Jet Fuel Antioxidant, Phenol Ortho-Alkylation

INTRODUCTION

Topanol A prevents gum formation in fuels during the storage periods. The gum has formed clog carburetor, injector orifices and filters in the engine, causing accumulation of contamination in the input system and reduction of octane in the fuel (1-3). According to ^1H NMR spectroscopy,

the main component of the additive is 2,6-di-t-butylphenol. In addition, it also contains small amounts of other mono and dialkyl substituted phenols. The specifications of Topanol A used in Iranian refineries are given in Table 1.

*Corresponding author

Ali Mehdizadeh

Email: mehdizadeha@ripi.ir

Tel: +98 21 4825 6033

Fax: +98 21 4473 9752

Article history

Received: May 12, 2018

Received in revised form: November 20, 2018

Accepted: December 1, 2018

Available online: August 7, 2019

DOI: 10.22078/jpst.2018.3299.1526

<http://jpst.ripi.ir>

Table 1: Specifications of Topanol A.

Main chemical ingredient	2,6-di-t-butylphenol
Color	Brownish yellow
Density at 4°C	0.93 g/mL
Viscosity at 40°C	8.1-10 (cSt)
Melting point	11 °C
Flashpoint	100 °C
Consumption amount	1.6 10 ⁻⁵ × l/l fuel

Phenol alkylation is usually carried out using an alkylating agent in the presence of a catalyst. The alkylating agents are typically alcohols or olefins, and some of the corresponding catalysts include Lewis acid catalysts, inorganic and/or organic acids, ion exchange resins, and solid supports (3). The main three industrial phenol alkylation processes are:

a. Liquid phase alkylation

In this process, the alkylating agent is added to a solution or suspension of the catalyst in phenol, and the catalyst is removed from the reaction media and neutralized after the product is formed.

b. Fixed bed liquid phase alkylation

The reactants pass over the catalyst through externally cooled tubular reactors. The catalysts include Lewis acids such as AlCl₃, BF₃, and Al(OPh)₃, protonated acids such as HF, H₂SO₄, and H₃PO₄, and p-toluene sulfonic acid or ion exchange resins.

c. Vapor phase alkylation

Phenol and an alkylating agent such as alcohol or olefin agent are heated in a fixed bed at 300-400 °C. Some of the catalysts with high thermal stabilities used in this method include fixed beds such as Montmorillonites, zeolites, and metal oxides (2). Phenol alkylation usually yields a mixture of ortho and para isomers. However, ortho-alkylation may be carried out using the appropriate reaction temperature, pressure, and catalytic conditions (4).

The selective ortho-alkylation of phenols is

achieved with aluminum triphenolate (Al(OPh)₃). Moreover, solid catalysts such as acidic ion-exchange resins or sulfonated polystyrenes, aluminum oxide or zeolites are also suitable.

The most industrially important method for ortho-alkylation of phenols was developed independently by researchers in Ethyl Corporation and Bayer A.G. Moreover, both groups used aluminum triphenolate as the catalyst (5-9). In addition, this method is a batch process in which aluminum is added to molten phenol in a stainless steel pressure reactor. The contents of the reactor are then heated to 120-180 °C for 0.5-1 hour during which aluminum forms aluminum triphenolate in situ by dissolving in phenol and liberating hydrogen gas, followed by cooling the reaction medium to 100 °C, releasing the hydrogen gas and injecting liquid isobutylene. The pressure initially increases to 15-20 atm, and then drops as isobutylene is used (Figure 1).

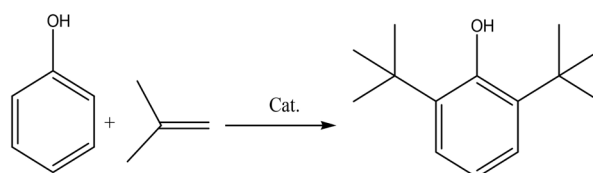


Figure 1: Ortho-alkylation of phenol.

The reaction is finally over in about 3 hours. Using a 1:2 molar ratio of isobutylene to phenol gives the percent product compositions in Table 2 of 2,6-di-t-butylphenol.

Table 2: Percent composition of the reaction products of phenol and isobutylene by Bayer process using 1:2 molar ratio of alkene to phenol.

Compound	Percentage (%)
Phenol	0.6
2-t-butylphenol	1.7
4-t-butylphenol	0.2
2,6-di-t-butylphenol	77.2
2,4-di-t-butylphenol	0.9
2,4,6-tri-t-butylphenol	19.4

The selectivity of this reaction to ortho isomer seems to be due to the formation of a strong acid complex (b) by the interaction of aluminum phenolate (a) and olefin with each other. The electrophilic substitution of the alkylating agent on the aromatic ring will then take place on the ortho position due to steric hindrance of the intermediate complex. Moreover, proton exchange with phenol will regenerate the catalyst and terminate the reaction (Figure 2) (10).

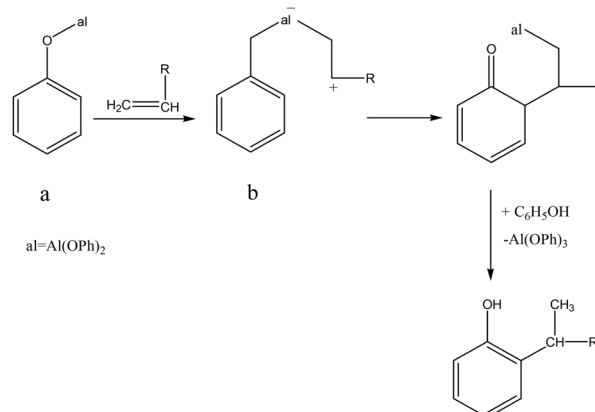


Figure 2: Mechanism of phenol ortho-alkylation using an olefin as the alkylating agent and $\text{Al}(\text{OPh})_3$ as the catalyst.

By considering the amount of 2,6-di-*t*-butylphenol produced in the Bayer process, this process was selected for lab scale synthesis of Topanol A. Thus, the product has been synthesized via ortho-alkylation of phenol using 2-methylpropene (isobutylene) or Butane-Butene Raffinate (BBR) alkylating agent and aluminum phenolate catalyst in bench and pilot plant scales and characterized by ^1H NMR spectroscopy. The antioxidant efficiency of formulations prepared using this product has been verified by the central quality control laboratory of the National Iranian Oil Refining and Distribution Company (NIORDC).

EXPERIMENTAL PROCEDURE

Syntheses were performed using explosion proof equipment. In addition, lab scale experiments were carried out in a 2 L, Buchi pressure reactor equipped with a digitally controlled pressure, temperature. The stirring rate, cooling coil and a thermal jacket was used in lab syntheses. The optimal lab scale conditions were applied in pilot plant preparations of Topanol A with minor modifications. Pilotscale reactions were carried out in a SS 316, 100 L pressure reactor (Disal Co., Iran) equipped with digitally controlled pressure and temperature, magnetic drive stirrer, explosion proof electric motor, cooling coil, and thermal element (Figure 3). The products were characterized by ^1H NMR spectroscopy using a Bruker AVANCE 500 MHz spectrometer.

Moreover, commercial grade phenol was obtained from Fluka Chemical Co. Aluminum (5010, 97.45%, Aluminum Pars Co., Iran) sheets were filed into a powder. The composition of aluminum sheets and percent distribution of different mesh sizes of the powder are shown in Tables 3 and 4 respectively. 2-methylpropene (isobutylene, > 99.5% pure) gas was obtained from Sigma Aldrich Chemical CO. Butane-Butene Raffinate (BBR) was supplied by Arak Petrochemical Complex. The composition of BBR is shown in Table 5. Isobutylene and BBR were collected in pressure vessels and injected into the reactor by nitrogen gas pressure. Nitrogen gas was obtained from Roham Gas Co. (Iran). Commercial grade Topanol A, ASA (antistatic additive) and ATK (Aviation Turbine Kerosene) jet fuel were provided by Tehran Oil Refinery.

Table 3: Composition of aluminum sheets.

Metal	Al	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Other
composition (%)	97.45	0.40	0.70	0.25	0.20	0.40	0.15	0.30	0.10	0.05

Table 4: Percent distribution of different mesh sizes of Al powder.

Mesh size	Percentage(%)
2	6
25	2
30	3
50	36
70	32
80	1
100	10
140	6
Over 140	4

Table 5: Composition of BBR.

Compound	Composition (%)
Isobutylene	65 min
1- butene	20 max
n and isobutylene	4.96 max
C ₃ cut	0.23 max
Trans 2-butene	7.48 max
Cis 2-butene	3.03 max
1,3-butadiene	0.3 max



Figure 3: 100 L pressure reactor (Disal Co., Iran) used for pilot scale preparation of Topanol A
General procedure for preparation of Topanol A.

Aluminum (1 wt. % of phenol) was added to phenol in a stainless steel pressure reactor. The contents of the reactor were then heated to 170 °C and maintained at that temperature for an hour during which aluminum formed aluminum phenolate (Al(OPh)₃) by dissolving in phenol and liberating hydrogen gas. The reaction mixture was then cooled to 50 °C, and the hydrogen gas released was carefully and slowly released. Isobutylene gas collected in a stainless steel pressure vessel was then quickly injected into the reactor forced by nitrogen gas pressure. The reaction mixture was then heated to 110 °C in 30 minutes and maintained at that temperature for the next 3 hours. The pressure initially increased to 200-300 psi, and then slowly dropped as isobutylene was consumed.

Upon the completion of the reaction, the mixture was cooled to 50 °C in about 15 minutes. Nitrogen gas was released from the reactor, and the product was removed as oil, which was washed with distilled water and 1% aqueous NaOH solution to remove excess phenol as well as impurities such as monoalkylphenol and dried on anhydrous MgSO₄ (11).

Synthetic Procedure for Topanol A in Pilot Plant Scale

The same procedure as that used for the lab scale preparation of Topanol A was used in 100 kg pilot plant scale. However, given the requirements for up scaling of the reaction, the following modifications were made.

a. Isobutylene addition rate: Due to safety considerations and in order to avoid overheating of the reaction mixture, isobutylene gas had to be

injected slowly within a period of half an hour such that the temperature of the reaction mixture was kept below 50 °C, and the pressure in the reactor did not exceed 310 psi during the addition.

b. Reaction time: The reaction mixture required a longer time (maximum of 2 hours) to reach the reaction temperature after the addition of isobutylene gas because of large reaction volume. Accordingly, the time required for cooling the reaction mixture to ambient temperature prior to release the excess nitrogen gas and removing the product was longer in the pilot scale (maximum of 50 minutes).

RESULTS AND DISCUSSION

The reaction products in all the cases were characterized by ¹H NMR spectroscopy. The ¹H NMR spectroscopic data for the products prepared in lab and pilot plant scales using commercial isobutylene are in complete agreement with those of commercial Topanol A (Table 6). However, the sample prepared using BBR showed impurities since BBR contains only about 70% isobutylene and ¹H NMR spectroscopy is not a reasonable criterion for the evaluation of this particular synthetic compound. Nevertheless, the quality control tests carried out to compare authentic and synthetic Topanol A samples. The tests indicated the compatibility of all Topanol A samples synthesized in this work regardless of the used alkylating agent.

Table 6: ¹H NMR spectroscopic data of the synthetic Topanol A using commercial isobutylene.

Proton Type	Peak Shape	Chemical Shift (ppm)	Number of protons	Integration
Aromatic	multiplet	6.6-7.3	3	1.7
Phenolic OH	broad singlet	5.1	1	0.5
t-butyl group	singlet	1.2	18	10.2

Antioxidant Quality Control Tests

As previously indicated, fuel antioxidants prevent gum or sludge. The efficiency of fuel antioxidants is evaluated via a set of tests collectively known as Full Test by the central quality control laboratory of the National Iranian Oil Refining and Distribution Company (NIORDC).

Fuel samples were prepared using equal amounts of the commercial and synthetic Topanol A along with other necessary additives, and the prepared formulations were subjected to Full Test in order to compare the synthetic and commercial samples. The formulations prepared and tested are shown in Table 7. The synthetic and commercial additives including Topanol A and ASA (antistatic additive) were blended in ATK fuel prior to carrying out the tests. The concentrations of Topanol A and ASA were 16×10^{-6} and 9×10^{-7} l/liter of fuel respectively.

Table 7: Formulations prepared.

Entry	Code	Topanol A type
1	A	Commercial
2	B	Synthetic (lab scale)
3	C	Synthetic (pilot plant scale)
4	D	Synthetic (using BBR as the alkylating agent)

The results of quality control tests of the prepared Topanol A samples are given in Table 8.

Table 8: Results of quality control tests of prepared Topanol A samples.

Test	Allowable limits	Formulation A*	Formulation B	Formulation C	Formulation D	ASTM Method
Oxidation Stability - Filter Pressure (kPa) - Tube Deposit Rating	Max. 3.3 < 3	0 2	0 < 2	0 < 2	0 < 2	D-3241
Conductivity (pS/m)	50-450	430	360	390	380	D-2624
Flash Point (°C)	Min. 38	46	47	46	46	D-56
Density at 15 °C (kg/m ³)	775-830	812.3	812.3	811.0	810.0	D-1298
Kinematic Viscosity at 20 °C (cSt)	Max. 8	4.44	4.43	4.40	4.42	D-445
Existent Gum (mg/100 mL)	Max. 7	3	2.4	4.2	4.2	D-381
Total Sulfur (wt.%)	Max 0.3	0.0070	0.0059	0.0045	0.0050	D-1266
Neat Heat of Combustion (MJ/kg)	Min. 42.8	43.045	43.095	43.107	43.109	D-1405
Aromatics (Vol.%)	Max. 25	20.1	20.1	20.1	20.1	D-1319
Total Acid Number(mgKOH/g)	Max. 0.015	0.0015	0.002	0.0016	0.0016	D-3242
Freezing Point (°C)	Max. -47	-63	-64	-63	-63	D-2386
Smoke Point (mm)	Min. 25	26	27	26	26	D-1322

*Formulation A contains authentic Topanol A

Formulations B and C have been prepared using a synthesized Topanol A in lab and pilot plant scales respectively. Sample D has been prepared using a synthesized Topanol A in the lab by BBR as the alkylating agent.

As observed in Table 7, the three formulations prepared using lab and pilot plant scale samples as well as the formulation prepared using Topanol A synthesized in lab scale by BBR as the alkylating agent (formulations B, C, and D respectively) meet the corresponding specifications with regards to

the antioxidant efficiency and are all comparable with the formulation prepared using the authentic Topanol A sample.

CONCLUSIONS

A jet fuel antioxidant has been synthesized in lab and pilot plant scales by selective ortho-alkylation of phenol using pure isobutylene gas and aluminum phenolate as the catalyst. Butane-Butene Raffinate (BBR) from Arak Petrochemical Complex has also been used as an alternative and cheap alkylating agent. In addition, commercial grade aluminum

supplied from local sources has also been used in the preparations. The application of commercial starting materials makes the process economically advantageous. In addition, ^1H spectroscopy has been used to characterize the synthetic samples. The synthesis has also been successfully carried out in 100 kg scale. The antioxidant samples synthesized in the lab and bench scales have then been formulated in ATK jet fuel along with an antistatic additive (ASA). The resulting formulations and the prepared formulations using authentic antioxidant have been evaluated in the quality control tests under identical conditions. The results indicate a reasonable efficiency for the synthetic antioxidants compared with the authentic commercial Topanol A sample using pure isobutylene gas or BBR.

NOMENCLATURES

ASA	: Antistatic Additive
ATK	: Aviation Turbine Kerosene
NIORDC	: National Iranian Oil Refining and Distribution Company
BBR	: Butane-Butene Raffinate

REFERENCES

- Bernabeia M., Bocchinfusa G., Carrozzob, P., and De Angelis C., "Determination of Phenolic Antioxidants in Aviation Jet Fuel," *Journal of Chromatography A*, **2000**, 871, 235-241.
- Pradelle F., Braga S. L., Rosa A., Martins F. A., and et al., "Gum Formation in Gasoline and Its Blends: A Review," *Energy and Fuels Journal*, **2015**, 29, 7753-7770.
- Beaver B., Gao L., Burgess-Clifford C., and Sobkowiak M., "On the Mechanisms of Formation of Thermal Oxidative Deposits in Jet Fuels. Are Unified Mechanisms Possible for Both Storage and Thermal Oxidative Deposit Formation for Middle Distillate Fuels?" *Energy and Fuels Journal*, **2005**, 19, 1574-1579.
- Degnan T. F., Smith C. M., and Venkat C. R. "Alkylation of Aromatics with Ethylene and Propylene: Recent Developments in Commercial Processes," *Applied Catalysis A: General*, **2001**, 221, 283-294.
- Ullmann F., Wolfgang G., Yamamoto Y. S., Campbell F. T., and et al., "Ullmann's Encyclopedia of Industrial Chemistry," VCH Publishers, **1985**.
- Titze-Frech K., Ignatiev N., Uerdingen M., Schulz P. S., and Wasserscheid P., "Highly Selective Aromatic Alkylation of Phenol and Anisole by Using Recyclable Brønsted Acidic Ionic Liquid Systems," *European Journal of Organic Chemistry*, **2013**, 30, 6961-6966.
- Kolka A. J., Napolitano J. P., Filbey A. H., and Ecke G. G., "The Ortho-alkylation of Phenols," *Journal of Organic Chemistry*, **1957**, 22, 642-646.
- Ecke G. G. and Kolka A. J. "Phenol Alkylation Process" US Patent, 2 831 898, **1958**.
- Stroh R. and Seydel R., "Verfahren Zur Kernalkylierung Von Hydroxylgruppenhaltigen Aromatischen Verbindungen," DT Patent, 944 014, **1954**.
- Stroh R., Seydel R., and Hahn W., "Phenol Alkylation Process" US Patent, 3 051 762, **1962**.
- Hahn, W. "Process for Production of Ortho-substituted Phenols" US Patent, 3 290 389, **1966**.
- Von Dozent D. and Gompper R. "Beziehungen Zwischen Struktur und Reaktivität Ambifunktioneller Nucleophiler Verbindungen," *Angew. Chem.*, **1964**, 76, 10, 412-423.
- King J. F., Matthews C. W., and Batman E. S. "Phenol Alkylation Process," US Patent, 4 870 216 A, **1988**.