

## Effect of Antioxidants on degradation of Furfural

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### ABSTRACT

Solvent extraction processes are the backbone of lube base stocks production in the refineries for the last few decades. The solvent processes are employed to remove aromatics from lube distillate. Among the solvents used for extraction, Furfural and N-Methyl Pyrolidone (NMP) are most prominent and are being used presently. However, solvent loss and hence makeup are inherent with these solvent extraction processes. Traditionally, these losses are seen as evaporation and handling loss and not as degradation loss. The degradation of furfural results in not only solvent loss but make the process less efficient.

To counter degradation of furfural, the present study has been taken up. The degradation occurs primarily due to oxidation under process conditions. Due to oxidation, efficiency of solvent mixture diminishes with time and hence the raffinate yield and quality of the product also deteriorates. Therefore, this study has been conducted to reduce the degradation of furfural with antioxidants. The antioxidant not only prevents the oxidation of furfural but also enhances the yield and quality of raffinate.

In this study, two commercially available antioxidants have been studied. The antioxidants are investigated for furfural oxidation in the temperature range of 40°C to 130°C and then extrapolated to process conditions using the degradation rate constant. The impact of antioxidants on furfural degradation was studied by determination of change in Total Acid Number (TAN) for pure furfural and for furfural with various concentrations of antioxidants at different temperatures. One of the antioxidant is found to be effective in retarding the oxidation of furfural. The same can be implemented at refineries to minimize furfural loss and make the furfural extraction process more efficient including prevention of corrosion in the process equipments.

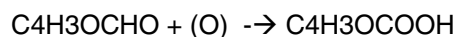
### KEYWORDS:

Furfural, antioxidant, degradation, extraction, lube base-stock

### INTRODUCTION

Furfural is known solvent for extraction of aromatics from lube distillates. In addition, it has a number of industrial uses including the manufacture of furans, tetrahydrofuran etc. Associated problem with the use of furfural is tendency to oxidize in the presence of atmospheric oxygen or air to form oxidation products such as furoic acid, formyl acrylic acid or formic acid, which upon further heating forms furfural acidic polymers. The oxidation products and the polymers are undesirable because they lead to a number of problems including corrosion of metal equipment and deposition of corrosion byproducts and acidic polymers on equipment surface. This leads to serious operational problems, such as restriction in flow of fluids. Due to leakage, storage and dissolved air in the system, it is extremely difficult to prevent air from contacting the furfural during manufacturing, storage and transportation. All of these factors, alone or in combination reduce the effectiveness of the end use of the furfural as a solvent in petroleum refining. In furfural extraction process, the some part of the process operated at elevated temperature of the order of 220°C. At elevated temperature some furfural is lost by acid and resin formation. Such loss should obviously be kept as low as possible.

### THEORY



Furfural normally gets oxidizes to form acid and the purity of furfural is reduced with time. The impact of antioxidants on furfural degradation was studied by determination of change in Total Acid Number (TAN) for pure furfural and for furfural with various concentrations of antioxidants at different temperatures. In this approach, the acid formed is neutralized with standard potassium hydroxide with respect to time and the amount of potassium hydroxide consumed indicates that the amount of acid formed. The amount of furfural degraded evaluated by amount of acid formed.

## EXPERIMENTAL PROCEDURE

### PREPARATION OF TITRANT

A standard KOH solution is used as the titrant. For the preparation of KOH solution, 1g KOH flakes are added to 1L Iso propyl alcohol. Then the mixture is gently boiled till all the flakes are completely dissolved. Then it is allowed to settle for about 48 hours. After 48 hours the standard KOH solution is prepared which is then filtered through a piece of cotton. Subsequently, the KOH solution is standardized with potassium hydrogen thalate solution.

### TITRATION SOLVENT

The titration solvent is a mixture of Isopropyl alcohol, toluene and water in the volume proportion of 100:95:5 is used as a titration solvent.

### STUDY ON FURFURAL OXIDATION

The experiments were carried out to demonstrate the tendency of furfural to oxidize at 40°C, 100°C and 130°C. A 200 ml of sample of furfural was placed in a flask and heated to desired temperature with continuous stirring. The total acid number of the furfural with or without antioxidants were determined at different time intervals and antioxidants composition.

### REACTION KINETICS OF FURFURAL DEGRADATION

The furfural degradation follows pseudo first order reaction (Zero order). The rate constants were estimated in all cases from the equation.

$$-dC/dt = (CA_0 - CA) / (tA - tA_0)$$

CA<sub>0</sub> - Initial concentration of furfural (gmole/litre)

CA - Concentration of Furfural at time tA (gmole/litre)

In the solvent recovery circuit of Furfural extraction process, temperature in the order of 220°C is being used to recover traces of solvent. So there is need to evaluate the reaction rate and rate constant upto 220°C to findout the degradation of furfural at higher temperatures.

According to Arrhenius equation, the kinetics of furfural degradation is represented through the plot of ln k against 1/T,

$$k = K_0 \cdot \exp(-E/RT) \text{ or } \ln k = \ln k_0 - (E/RT)$$

Where

K = Rate constant,

K<sub>0</sub> = Arrhenius pre-exponential factor,

E = Activation Energy,

### EVALUATION OF RATE CONSTANT AT 220°C

Arrhenius relation is used to evaluate the rate constant at 220°C. As per Arrhenius relation, the rate constant

$k = K_0 \cdot \exp(-E/RT)$ . By using of rate constant at 40°C, 100°C and 130°C, the plot between 1/T vs ln (k) drawn. From the plot the constant E/R and k<sub>0</sub> values were evaluated. From E/R and k<sub>0</sub> values, the rate constant at 220°C or 593K was determined. The details are shown in Table 1-3 and Figs. 1 to 6.

The experiments were conducted for pure furfural and with two commercially available antioxidants namely, antioxidant-1(AO-1) and antioxidant-2(AO-2) at various

## RESULTS AND DISCUSSION

The results of degradation of furfural with and without antioxidants (AO-1 & AO-2) are depicted in Figs.1 to 4. It is observed that at lower temperature, 40°C, the oxidation of furfural is reduced with both the antioxidants as indicated by the acid numbers (Fig.1). However, at 100°C, the AO-1 is found to be more effective at lower dosages, less than 300ppm compared to AO-2 (fig.2). At 130°C, AO-1 is found to be effective compared to AO-2. Fig.3 shows degradation of furfural without and with AO-1 at various dosages at 130°C.

The degradation rate also evaluated for Furfural degradation process at various temperature for AO-1 (Table-3). At 220°C, it is observed that AO-1 is found to retard the degradation of furfural to extent of 65% to 85% at the dosage level of 200ppm. This result is significant and therefore, antioxidant-1 may be employed to reduce oxidation furfural in the commercial furfural extraction units. This will minimize furfural loss significantly and also improves overall process economics.

## SUMMARY

The present study conducted to reduce the degradation of furfural using antioxidants. Two commercially available antioxidants were investigated for furfural oxidation in the temperature range of 40°C to 130°C and then extrapolated to process conditions using the degradation rate constant. Among the antioxidants studied, one of the antioxidant, AO-1 is found to be effective in retarding the oxidation of furfural at the dosage level of 200ppm. The same may be implemented at refineries after test runs to minimize furfural loss and make the extraction process more efficient.

## ACKNOWLEDGEMENT

Authors would like to thank Indian Oil R&D Management for granting permission to present this paper at ISFL-2008.

## REFERENCE

1.Heng Jiang, Hong Gong and Rui Wang, The screening of Antioxidants for furfural, Petroleum Science and Technology, 24:187-194,2006.

Table: 1 Evaluation of E/R value for pure furfural degradation

S.No	Temperature (K)	Rate Constant(K) gmoles/litre.hr	1/T	ln(K)
1	313	0.0053	0.00319	-5.2400
2	373	0.006	0.00268	-5.1159
3	403	0.0095	0.00248	-4.6564

Table : 2 Evaluation of E/R value for Furfural with 200 ppm of AO-1

S.No	Temperature (K)	Rate Constant(K) gmoles/litre.hr	1/T (k <sup>-1</sup> )	ln(K)
1	313	0.0009	0.00319	-7.0131
2	373	0.00092	0.00268	-6.9911
3	403	0.0031	0.00248	-5.7763

Table : 3 Effect of Antioxidant -1 (200 ppm) on the reduction in degradation  
Rate of furfural at various Temperature

S.No	Temperature(K)	% Reduction in degradation rate
1	373	85
2	403	67.37
3	593	66.82

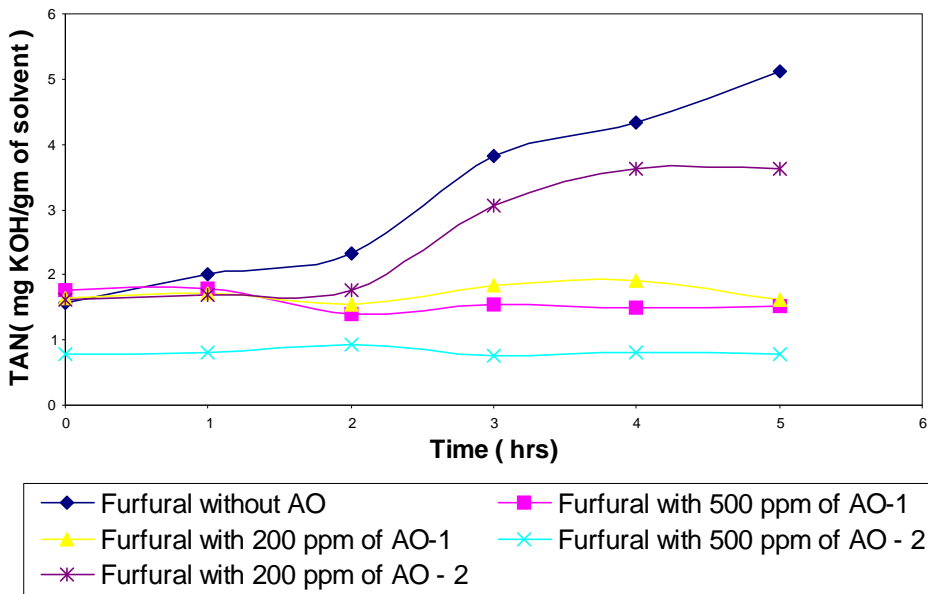


Fig. 1 Comparative study on degradation of furfural with or without antioxidants at 313°C

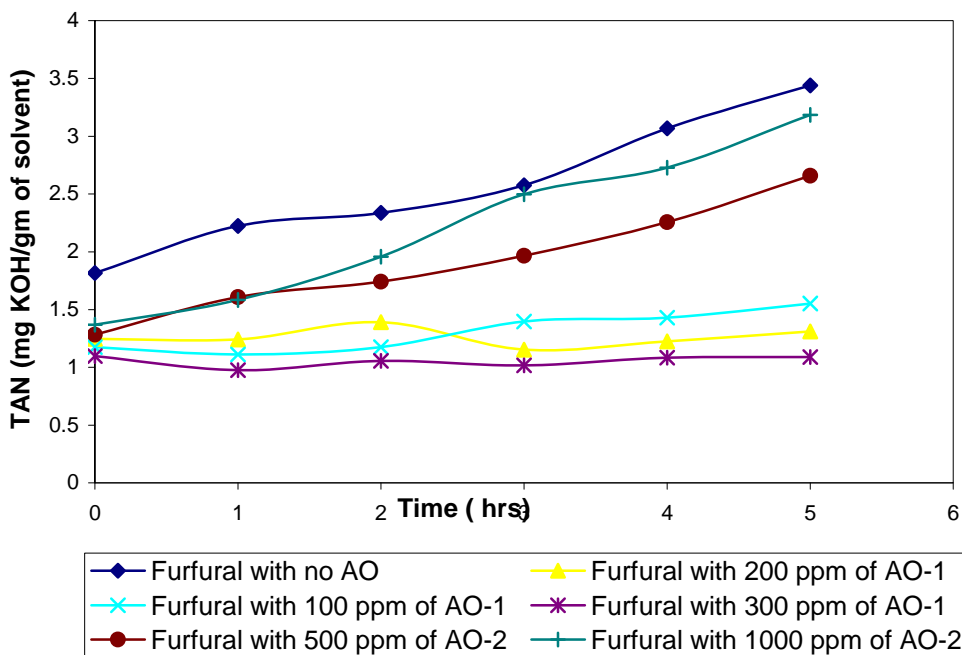


Fig.2 Comparative study on degradation of furfural with or without antioxidants at 373°C

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Fig. 3 Comparative study on degradation of furfural with or without Antioxidants at 403°C

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Fig.4 Effect of AO-1 on furfural degradation at various temperatures

Fig. 5 Evaluation of E/R value for neat furfural degradation

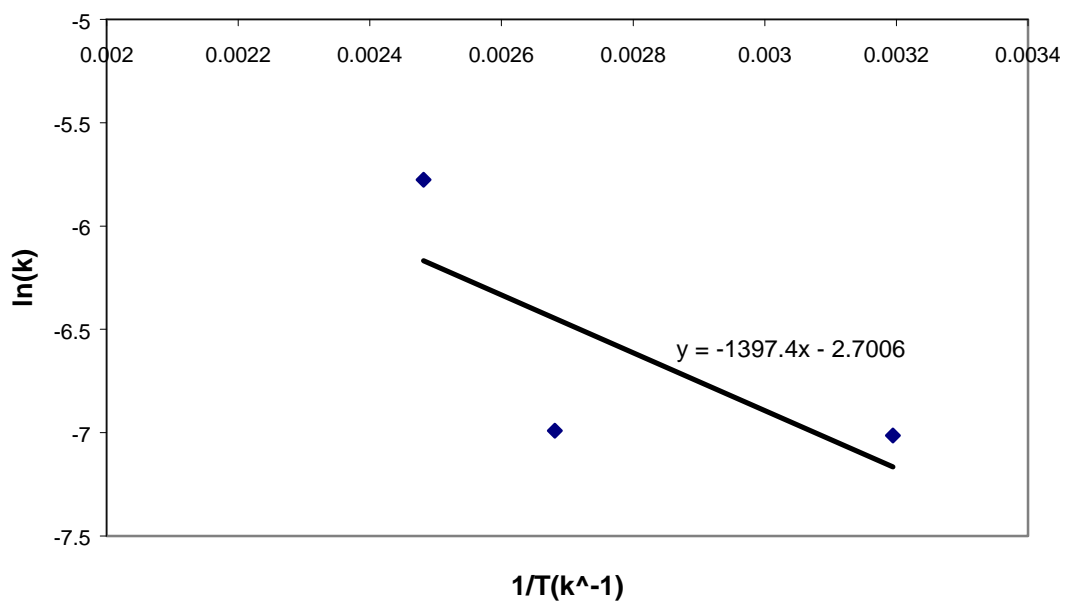


Fig. 6 Evaluation of E/R value for furfural +200ppm of AO-1