



Reactive thermal hazards of irradiated tributyl phosphate with nitric acid

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ABSTRACT

Red oil incidents reported worldwide are attributed to the reactive thermal reactions between Tributyl phosphate (TBP) and nitric acid. The vigor of thermal behavior may be influenced by various factors including irradiation, presence of metal nitrates etc. This work is focused to study the influence of irradiation on the reactive thermal behavior of 30% TBP with varying strengths of HNO₃ for the first time. The Accelerating Rate Calorimetry (ARC) studies reveal that irradiated 30% TBP reacts exothermically with 4 mol/L–16 mol/L HNO₃ and contributes to rise in system pressure. A lower onset temperature for exothermic reaction was noticed in irradiated TBP compared to the non-irradiated 30% TBP with acid. From the Zero-Order kinetic model, the TMR_{ad} for irradiated and non-irradiated TBP 4 mol/L HNO₃ system was been determined for thermal hazard assessment. FT-IR, NMR and GC–MS characterization of the residues of ARC clearly suggest that conversion of butanol to butanoic acid is the exothermic red-oil forming reaction.

1. Introduction

Tributyl phosphate (TBP) is used as an extractant of choice for nuclear fuel reprocessing in the Plutonium Uranium Extraction (PUREX) process over five decades. 30% TBP in n-dodecane is generally used as an extractant where uranium and plutonium are extracted and separated from fission products from the spent fuel [1]. In spite of positive attributes of TBP such as its good extraction efficiency, better decontamination from fission products etc., TBP undergoes decomposition due to high radiation and temperature leading to the formation of reactive red oil at temperatures exceeding 130 °C [2]. TBP also finds extensive applications as plasticizer, solvent in inks, synthetic resins, gums, adhesives etc. [3,4]. Five major red oil related accidents were reported worldwide due to this unfavourable condition which has caused widespread damage to the reaction vessels and structures. Among those reported Savannah River (1953) and Toms (1993), were the major accidents. In many of them, TBP with its degradation products, nitrates derived from nitric acid and heavy metals were involved [5].

Several reasons were attributed to these incidents; one reason was the entry of organic layer into vessels where uranyl nitrate solutions were being heated to moderately high temperatures [6]. The oxidation of TBP and its decomposition products are dependent on several parameters, such as temperature, acid concentration, the length of time of

contact between the organic and aqueous phases, the efficiency of contact (mass transfer), and radiolysis [7]. It was reported in literature that a compound which is subjected to irradiation will undergo structural and mechanical changes [8]. Scanning electron microscope studies on β-glucan and crotoxin suggested that increase of the dosage of gamma irradiation (⁶⁰Co) would lead to loss of their behavioral effects due to its deformation into smaller granules [9,10]. Irradiation would cause a shift of the onset temperature of degradation leading to changes in chemical and physical properties of a system when it is influenced by radiation [11].

Understanding into reactive hazard nature of TBP and its related degradation compounds in the chemical processing facility of fuel recycling is essential to arrive at safety margins. Gao Yang et al. [12] studied the Irradiation stability of the 30% TBP/n-dodecane solution with samples exposed to ⁶⁰Co γ rays or α particle from plutonium dissolved in the organic phase. Using GC–MS analysis of the irradiated organic phase, it was stated that the two main degradation products Dibutyl Phosphate (DBP) and Monobutyl Phosphate (MBP) were obtained. Results show that influence of the irradiation and HNO₃ concentration on the amount of DBP was much larger than that of MBP. The DBP yield increased with the irradiation dose, and the DBP yield at low HNO₃ concentration was larger than that at high HNO₃ concentration.

Chandran et al. [13] reported that 1.1 M HNO₃ TBP in n-Dodecane

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Nomenclature			
H	Enthalpy of the reaction (J)	m_s	Mass of the solvent (g)
ΔH_r	Heat of the reaction (J/mol)	C_{ps}	Specific heat of the sample ($Jg^{-1}K^{-1}$)
ΔT_{ad}	Adiabatic temperature rise ($^{\circ}C$)	m_b	Mass of the bomb (g)
ΔT_{ab}	Absolute temperature rise ($^{\circ}C$)	C_{pb}	Specific heat of the bomb ($Jg^{-1}K^{-1}$)
ϕ	Thermal inertia (-)	A	Arrhenius pre-exponential coefficient (-)
		E_a	Activation energy in (J/mol^{-1})
		R	Gas constant ($8.314 Jmol^{-1}K^{-1}$)

and n-octane did not show any accelerated decomposition but 8 mol/L HNO_3 equilibrated solutions of 1.1 M TBP/n-Dodecane had shown lesser excursions in temperature and pressure due to the lower concentration of TBP and nitric acid present in these systems. Krishnamurthy and Sipahimalani [14] reported that the nitric acid present in the TBP phase enhances considerably the irradiation-induced decomposition in the TBP- HNO_3 system. When the irradiation dosage was large, C_4H_9 , OH, H, NO, NO_2 , etc., are anticipated and took part in secondary reactions forming higher molecular weight compounds which include dimers, trimers and other polymeric species. This was indicated by the numerous peaks observed in the gas chromatogram. Qi et al. [15] used C80 micro calorimeter technique to investigate the thermal decomposition of TBP- HNO_3 system. Results obtained reveal that concentration of nitric acid greatly influenced thermal hazard of the system by direct reactions leading to thermal runaway at lower temperatures. Red oil related accidents due to thermal runaway are one of the major safety issues faced by recycling facilities. In a runaway reaction, the heat generated within the system tends to exceed the heat removal capacity. This can further initiate secondary reactions leading to an explosion [16,17].

Our previous studies on irradiated TBP with various dosage of irradiation revealed that the bound water molecules of TBP were gradually lost with the increase in dose (time) of irradiation [18]. Investigations on thermal reactivity between 30% TBP (without irradiation) with nitric acid confirmed that oxidation of butanol to butanoic acid was the red oil forming self-heating reaction [19]. Further, studies on effect of diluents on thermal behavior of TBP with acid showed reactive thermal hazards due to notable pressure rise rather than the temperature excursion. It is suggested that oxidation of butanol to butanoic acid was the main reason behind exothermicity [20].

Extensive research has been carried out on TBP, TBP- HNO_3 systems as described above, but the studies on influence of irradiation on red oil formation with TBP- HNO_3 systems are not addressed well. The present study deals with the Accelerating Rate Calorimetric (ARC) studies of irradiated TBP- HNO_3 systems, safety limits for the accident prevention in fuel recycling facilities and chemistry behind the red oil formation was established using analytical facilities such as FT-IR, NMR and GC-MS.

2. Methods and materials

a. Materials

TBP and n-dodecane were obtained from Indira Gandhi Centre for

Atomic Research (IGCAR); Kalpakkam, India, nitric acid used in these studies was of analytical grade obtained from Aldrich Chemicals.

b. Preparation of 30% TBP

TBP obtained from the IGCAR Kalpakkam was mixed with n-dodecane to prepare 30% TBP for ARC studies. The mass % of TBP, n-dodecane and HNO_3 is 15, 35 and 50%. TBP-n-dodecane mixture (0.5 g) and HNO_3 (0.5 g) is loaded into ARC sample bomb in 1:1 ratio. Sample purity and source of the same is given in Table 1. The initial mixture contains TBP-15%, n-dodecane-35% and nitric acid-50%.

c. Methods

2.1. Irradiation Chamber

Irradiation experiments were carried out using ^{60}Co source in an irradiation chamber supplied by Board of Radiation and Isotope Technology (BRIT), Mumbai with an irradiation flux of 2.36 KiloGray/h (0.236 MR/h) [18]. The exposure rate due to ^{60}Co gamma source of the chamber was 2.36 KiloGray/h (0.236MR/h) at room temperature. Each time 5 ml of TBP samples in glass tubes were irradiated inside the g-chamber for 21 h for attaining 5 MR radiation. The gamma source used for the irradiation experiments is well concealed fixed source. In the irradiation chamber, only the sample compartment is mobile and the gamma source is fixed and as a result, the radiation field outside the chamber maintained within limits by adopting good housekeeping practices. Personal monitoring dosimeters are worn while carrying out the experiments and the radiation field is continuously monitored by Area Gamma Monitors (AGM). The irradiated TBP samples from the irradiation chamber were used for the Accelerating Rate Calorimetric studies.

2.2. Accelerating rate calorimeter (ARC)

ARC illustrated by Fig. 1 procured from Thermal Hazard Technology, UK, was used in our studies to assess the behavior of irradiated TBP with concentrated HNO_3 . The sample bombs used were made of Hastelloy. The sample bomb was fitted to the lid section of the calorimeter assembly by a Swagelok fitting and to a pressure line that led to the pressure transducer. A thermocouple was attached to the side clip of the bomb and the lid of the calorimeter positioned on the base section. The calorimeter consisted of three separate thermal zones sealed with an explosion proof containment vessel [21,22].

In this study, ARC experiments were carried out using the heat-wait-search mode. The starting temperature and the calorimetric detection

Table 1
Purity and source of the samples.

S.NO	Chemical Name	Source	Purification Method	Mole Fraction Purity (%)	Analysis Method
1	^a TBP	^b IGCAR	Not purified – used as such	100	^c FTIR, Mass spectroscopy (^d NIST)
2	n-Dodecane	^b IGCAR	Not purified – used as such	100	FTIR, Mass spectroscopy
3	Nitric acid	^e Sigma Aldrich	Redistillation	99	Trace metal Basis

^a TBP – Tributyl phosphate.

^b IGCAR – Indira Gandhi Centre for Atomic Research.

^c FT-IR – Fourier-Transform Infra-Red Spectroscopy.

^d NIST - National Institute of Standards and Technology research library.

^e Sigma Aldrich - <https://www.sigmaaldrich.com/catalog/product/aldrich/225711?lang=en®ion=IN>.

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