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Synthesis of N,N,N′,N′-Tetraoctyl-3-oxapentane-1,5-diamide (TODGA) and Its Steam Thermolysis-Nitrolysis as a Nuclear Waste Solvent Minimization Method

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S Supporting Information

ABSTRACT: The amide based nuclear extractant, N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide (TODGA), was synthesized by an alternate route. A noncatalytic steam thermolysis and nitrolysis of TODGA was investigated in a SS 316 flow reactor as a nuclear waste solvent minimization method. All the reaction products of steam thermolysis and nitrolysis of TODGA were identified by using gas chromatography-thermal conductivity-flame ionization-mass spectroscopic detection techniques to get the complete mass balance. In the pyrolysis products, C_1-C_4 hydrocarbon gases, NOx, alkyl amines, and unconverted TODGA were characterized and quantified. The experimental data for the steam pyrolysis of TODGA was obtained in a temperature range of 550−1100 °C at overall atmospheric pressure. A continuous steam pyrolysis of TODGA in a SS 316 flow reactor over a temperature range of 850 to 1000 °C was found to be an irreversible, pseudo-first-order reaction with approximate activation energy of 123 kJ/mol. A comprehensive reaction network model was proposed to include the reaction mechanism of steam thermolysis of TODGA. The present experimental data and product's statistics of the steam nitrolysis of TODGA estimates that the possibility of the explosive runaway reactions during the nitration of TODGA at elevated temperatures is rare.

1. INTRODUCTION

In nuclear industry, the reprocessing of radioactive waste and recovery of the useful metals from irradiated spent fuel is mainly performed by solvent extraction methods. The UREX and PUREX processes are widely used to recover U and Pu from spent fuel by using tri-*n*-butyl phosphate (TBP) as an extractant.[1,2] In the post PUREX steps, the "high level waste" (HLW) is generated, which mainly contains bred actinides and long life radioactive fission products. Commonly, the HLW is vitrified and buried in nuclear geological repositories to allow the decay of radioactive metals such as ^{90}Sr, ^{99}Tc, and [137]Cs.[3] However, the transport of hazardous radionuclides in the form of their oxometallates (e.g., TcO_4^-) from the nuclear repositories to the environment and then to the living organisms through a food chain is of a severe risk, which necessitates the careful surveillance of nuclear repositories for a longer period.[4−8] To reduce such a long and obligatory surveillance period of nuclear repositories and for the sustainable development of nuclear energy, the partitioning of radioactive metals from HLW and their subsequent trans-mutation (P & T method) is being professed seriously, by several countries.[9−13] After the separation of radioactive actinides and lanthanides, the remaining residual solid waste can be vitrified and buried in subsurface repositories at much reduced risk and cost.[14]

To this end, the designing, synthesis, and extraction efficiency of some selective organic extractants for the separation of fission products from the HLW is actively investigated. TBP is the leading commercial extractant employed in the PUREX operations, for the last several decades.[15] However, the eliminated waste TBP and its analogues cannot be decomposed, and an enormous amount of phosphate bearing solid waste has to be managed at the end of its life cycle.[16−18] In addition, TBP has some drawbacks such as thermal and radiochemical instability under the operating conditions, the troublesome nature of its decomposition products, and its severe toxicity.[19−21] During the process of evaporation, to concentrate the aqueous waste or product nitric acid solutions, the dissolved or entrained TBP and its hydrolysis products, butanol is nitrated easily by HNO_3 and produces red oil (i.e., mixture of organic nitrates, nitrites, phosphates, alcohols, etc.) at above 130 °C.[22−24] Thermal decomposition of red oil in closed evaporators results in rapid pressurization due to the formation of N_2, O_2, H_2, CO, CO_2, N_2O, NOx, and hydrocarbon gases (C_1-C_4) and ultimately ends in explosive runaway reactions, which is often mentioned as a big source of worry.[25]

Recently, different groups of amides have been extensively studied as alternative extractants to the phosphate based solvents.[26−29] The completely incinerable N,N,N′,N′-tetraoc-tyl-3-oxapentane-1,5-diamide (TODGA) has shown high distribution ratio (D) for actinide (Ac) ions between HNO_3 and *n*-dodecane.[30−32] The applicability of TODGA is being

actively investigated by many separation scientists and nuclear engineers as an efficient mobile carrier to separate the actinides and lanthanides from HLW.[33,34] Also, the performance of TODGA for the actinide partitioning in a hollow-fiber supported liquid membrane was thoroughly evaluated as the most promising green extractant to replace the phosphates in nuclear reprocessing steps.[35−41] Since TODGA is unstable toward radiation, it readily degrades to N,N-dioctyl amine, N,N-dioctyl acetamide, N,N-dioctyl glycolamide, and N,N-dioctylformamide.[42] The interfacially active solvent-degradation products can diminish the solvent extraction performance. Thus, in the hydrometallurgical operations, after a certain number of extraction cycles, the solvent cleanup process will have to be carried out to discard the degraded TODGA, which may lead in the deposition of an enormous amount of low-level waste organic amidic solvents.[43−46] To overcome the future risk of massive deposition of the waste amides, we present here a noncatalytic continuous steam thermolysis process for the complete disposal of waste amidic extractants into eco-friendly gases. A number of publications dealing with the steam pyrolysis of hydrocarbons-naphtha-petroleum fractions are available in the open literature, but the reports on steam thermolysis of amidic extractants as a nuclear waste solvent management method are scarcely found, so far. The coke deposited on the inner wall of a typical thermal pyrolysis reactor causes an undesirable pressure drop and results in periodic shutdowns of pyrolysis plants for the carbon burnout.[47,48] An excess amount of steam in the steam pyrolysis process, however, avoids such carbon deposition and secures constant conditions for the continuous pyrolysis process.[49,50] Much of the work in this report is devoted to the process development, experimental studies, separation, identification, and quantification of all the pyrolysis products by chromatographic methods. Further, the overall kinetics and possible reaction mechanism of the steam pyrolysis of TODGA is proposed.

2. MATERIALS AND METHODS

2.1. Synthesis of TODGA. An alternate and cost-effective approach to the synthesis of TODGA was developed following a synthetic route shown in Figure 1. The present method eliminated the use of highly expensive raw materials like diglycolic acid and diglycolic anhydride.[36,51−53]
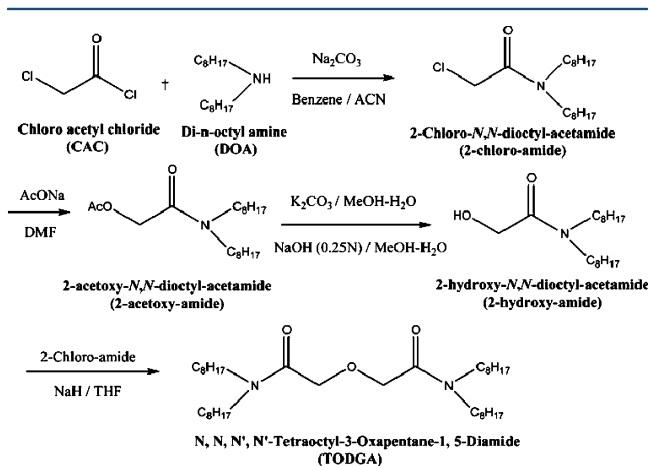

Figure 1. Synthetic approach to N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide (TODGA).

2.1.1. Synthesis of 2-Chloro-N,N-dioctyl-acetamide (2-Chloro-amide). Chloroacetyl chloride (1.65 cm³, 0.02 mol) was slowly added to a suspension of anhydrous sodium carbonate (6.5 g, 0.06 mol) in acetonitrile (50 cm³) at 0−5 °C and maintaining the temperature of the reaction mass between 0 and 5 °C. To this mixture, a solution of di-n-octyl amine (5 g, 0.02 mol) in benzene (20 cm³) was added dropwise over a period of 30 min. After the addition was over, the reaction mass was stirred for another 45 min at 50 °C at 600−700 rpm. An organic solvent was then distilled out at 27−30 °C under reduced pressure. The product was extracted from the residue with benzene (50 cm³) to separate out inorganic solids which were filtered and removed. The benzene extract was washed with 0.5 N HCl (30 cm³), 5% NaHCO₃ (30 cm³), and then by brine solution. The organic layer (benzene) was separated, dried over sodium sulfate, and distilled out at 27−30 °C under reduced pressure to get an oily mass. The oily product was then dissolved in diisopropyl ether (15 cm³) and was filtered to remove the insoluble part. A crude product (yield 88−90%, purity 95.8%) was isolated after removal of diisopropyl ether under the reduced pressure. In order to generate the standard product for spectroscopic analysis, the crude mass was purified through column chromatography using silica gel (230−400 mesh size) as packing material and 5% ethyl acetate in hexane (or petroleum ether 60−80) as mobile phase. A light yellow, viscous liquid with neat purity of 99.13% was obtained.

Density TLC (ethyl acetate-01 cm³:hexane-03 cm³) Rf 0.7, DSC (bp 208−210 °C), IR: ν = 2955 cm⁻¹ (C−H of CH₃), 2926 cm⁻¹ (ν_{as} C−H of CH₂), 2855 cm⁻¹ (ν_s C−H of CH₂), 1655 cm⁻¹ (C=O of amide), 1466 cm⁻¹ (CH₂ bending), 1122 cm⁻¹ (C−N str.), 1019 cm⁻¹ (C−O ether). MS (EI) m/z (%): 318 (100%) (M⁺, Cl³⁵), 320 (35%) (M⁺, Cl³⁷), 340 (80%) (M⁺+Na, Cl³⁵), 341.9 (25%) (M⁺+Na, Cl³⁷), 363 (10%) (M⁺+2Na, Cl³⁵), 365 (3%) (M⁺+2Na, Cl³⁷). ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS) δ 0.865 (6H, m), δ 1.286 (20H, s), δ 1.526 (4H, m), δ 3.250−3.281 (2H, t, J = 7.6 Hz), δ 3.30−3.33 (2H, t, J = 7.6 Hz), δ 4.05 (2H, s).

2.1.2. Synthesis of 2-Acetoxy-N,N-dioctyl-acetamide (2-Acetoxy-amide). Anhydrous sodium acetate (1.47 g, 0.017 mol) was added to a solution of 2-chloro-N,N-dioctyl-acetamide (5.0 g, 0.015 mol) in DMF (50 cm³) at 27−30 °C, and then the mixture was stirred at 70 °C for 3 h. DMF was distilled out from the reaction mass at 70 °C under reduced pressure, and the product was extracted with benzene (50 cm³), leaving behind unreacted sodium acetate and sodium chloride, which were separated by filtration. Removal of benzene at room temperature and reduced pressures produced the crude oily product (yield 95%, purity 97%). Column purification of the crude product (as described in the earlier section) using 7% ethyl acetate in hexane produced a faint yellow, viscous liquid with purity 99.83%.

TLC (ethyl acetate-01 cm³:hexane-03 cm³) Rf 0.5. DSC (bp 210−215 °C), IR: ν = 2956.20 cm⁻¹ (C−H of CH₃), 2927.08 cm⁻¹ (ν_{as} C−H of CH₂), 2856.01 cm⁻¹ (ν_s C−H of CH₂), 1754.01 cm⁻¹ (C=O of ester), 1670.81 cm⁻¹ (C=O of amide), 1466.49 cm⁻¹ (CH₂ bending), 1228.91 cm⁻¹ (C−N str.), 1081.04 cm⁻¹ (C−O ether). MS (EI) m/z (%): 342.1 (100%) (M⁺), 364.1 (95%) (M⁺+Na), 300.1 (70%) (M⁺-AC), 387.2 (10%) (M⁺+2Na). ¹H-NMR (500 MHz, CDCl₃, 25 °C, TMS) δ 0.860 (6H, m), δ 1.297 (20H, s), δ 1.51 (4H, m), δ 2.179 (3H, s), δ 3.123−3.159 (2H, t, J = 7.5 Hz), δ 3.286−3.317 (2H, t, J = 7.5 Hz), δ 4.7 (2H, s).

2.1.3. Synthesis of 2-Hydroxy-N,N-dioctyl-acetamide (2-Hydroxy-amide). To a cold solution (0–5 °C) of 2-acetoxy-N,N-dioctyl-acetamide (3 g, 0.0087 mol) in methanol (30 cm³) was added dropwise over a period of 15 min a solution of sodium hydroxide (0.35 g, 0.0087 mol) in water (3 cm³), and then the entire solution was stirred at the same temperature for 1 h. Methanol was then distilled out from the reaction mass at 27–30 °C under reduced pressure, and the product was extracted with benzene (30 cm³). The benzene layer was washed with 0.5 N HCl (10 cm³), 5% NaHCO₃, and brine (10 cm³) and then dried over sodium sulfate. Removal of benzene under reduced pressure produced a crude oily product (yield 95%, purity 98.8%). Purification of crude product was carried out through column chromatography using 7% ethyl acetate in hexane to produce faint yellow, viscous liquid with purity of 99.98%.

In an alternate approach, a solution of potassium carbonate (1.21 g, 0.0088 mol) in water (4 cm³) was added to 2-acetoxy-N,N-dioctyl-acetamide (1.0 g, 0.0029 mol) in methanol (20 cm³) and was stirred at 65 °C for 16 h. The isolation of the crude product (yield 96%, purity 98.3%) and the subsequent purification was as per the previous section.

Rf 0.6 (ethyl acetate-01 cm³:hexane-03 cm³). DSC (b.p 244–248 °C), IR: ν = 3411.82 cm⁻¹ (O–H str.), 2956.18 cm⁻¹ (C–H of CH₃), 2926.66 cm⁻¹ (ν_{as} C–H of CH₂), 2855.73 cm⁻¹ (ν_s C–H of CH₂), 1651.44 cm⁻¹ (C=O of amide), 1467.27 cm⁻¹ (CH₂ bending), 1402.66 cm⁻¹ (O–H bending), 1089.59 cm⁻¹ (C–N str.). MS (EI) m/z (%): 300.1 (100%) (M⁺), 322 (90%) (M⁺+Na), ¹H-NMR (500 MHz, CDCl₃, 25 °C, TMS) δ 0.864 (6H, m), δ 1.288 (20H, s), δ 1.536 (4H, m), δ 3.029–3.060 (2H, t, J = 7.5 Hz), δ 3.344–3.374 (2H, t, J = 7.5 Hz), δ 3.688–3.704 (1H, t, J = 4.0 Hz), δ 4.13 (2H, d, J = 4.0 Hz).

2.1.4. Synthesis of N,N,N′,N′-Tetraoctyl-3-oxapentane-1,5-diamide (TODGA). Sodium hydride (0.96 g, 0.02 mol) was added slowly to a solution of 2-hydroxy-N,N-dioctyl-acetamide (3.0 g, 0.01 mol) in THF (30 cm³) at 55–60 °C and stirred for 15 min. A solution of 2-chloro-N,N-dioctyl-acetamide (3.19 g, 0.01 mol) in THF (30 cm³) was then added slowly over a period of 15–20 min, and the reaction mass was stirred for 1 h at the same temperature. THF was removed by distillation under reduced pressure at 27–30 °C. To the remaining mass was added water (30 cm³), and the mixture was stirred for 10–15 min. The product was then extracted with benzene (60 cm³). The organic layer was washed with 0.5 N HCl (20 cm³) and 5% NaHCO₃ followed by brine wash and then dried over sodium sulfate. Benzene was removed under reduced pressure to get a light yellow, oily product (yield 96%, purity 98.5%). A 10% ethyl acetate and 90% hexane mixture was used as mobile phase for the column chromatography to purify the crude product. After chromatographic separation, TODGA was obtained with a neat purity of 100%.

TLC (ethyl acetate-01 cm³:hexane-03 cm³) Rf 0.3. DSC (b.p 310–320 °C), IR: ν = 2955.91 cm⁻¹ (C–H of CH₃), 2925.87 cm⁻¹ (ν_{as} C–H of CH₂), 2855.38 cm⁻¹ (ν_s C–H of CH₂), 1657.65 cm⁻¹ (C=O of amide), 1467.25 cm⁻¹ (CH₂ bending), 1121.79 cm⁻¹ (C–N str.), 1033.85 cm⁻¹ (C–O str.). MS (EI) m/z (%): 581.3 (100%) (M⁺), 603.3 (80%) (M⁺+Na), 626.5 (10%) (M⁺+2Na). ¹H-NMR (300 MHz, CDCl₃, 25 °C, TMS) δ 0.877 (12H, m), δ 1.268 (40H, s), δ 1.517 (8H, s), δ 3.149–3.199 (4H, t, J = 7.6 Hz), δ 3.264–3.315 (4H, t, J = 7.6 Hz), δ 4.309 (4H, s).

Density of synthesized TODGA was measured as 0.93 g/cm³ by using an Anton-Paar DMA-5000 densitometer, which was standardized by using dry air. All the chemicals and reagents were of AR grade, which were purchased from S. D. fine chemicals Pvt. Ltd., Mumbai. All the standards of gases (99.99% purity) were procured from Alchemie gases and chemicals Pvt. Ltd., Mumbai.

2.2. Steam Pyrolysis Setup. A laboratory scale steam pyrolysis setup is shown in Figure 2. The preheater-vaporizer
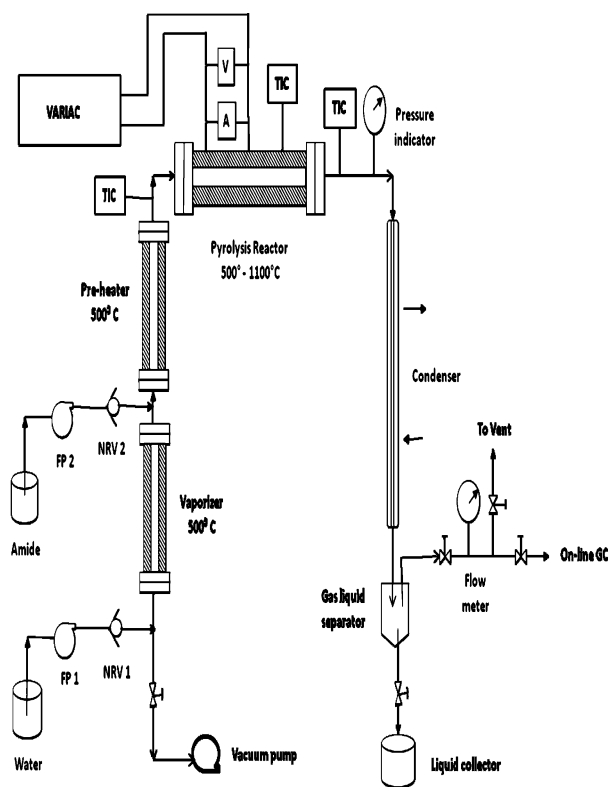

Figure 2. Schematic view of experimental setup for steam pyrolysis setup.

assembly (90 cm), incorporated with pyrolysis plug flow reactor (PPFR, 55 cm) was fabricated by using SS 316 tube (12 mm OD × 10 mm ID). The preheater–vaporizer assembly was wound by flexible heating tape, which can be electrically heated up to 500 °C. The pyrolysis reactor was wound by a flexible, ceramic beaded nichrome filament (1.2 KW) that was heated up to 1100 °C. The power supply to the ceramic beaded heater was monitored by a voltage stabilizer. The temperature of preheater–vaporizer assembly and that of a PPFR was separately controlled by two temperature regulators. The K-type thermocouples were used to measure the temperature of the reactor wall. An additional K-type thermocouple was connected at the exit of PPFR to measure the temperature of the reaction mixture. The entire reactor setup was compactly insulated by ceramic wool and encapsulated in aluminum foil to avoid the heat transfer to the surroundings. The PPFR was further equipped with a metal condenser (SS 316, 90 cm) and SS phase separator with chilled water cooled jacket.

The preheater and PPFR were heated up to the set temperature. A dual channel peristaltic pump with individual controls was used to feed distilled water and TODGA, simultaneously from their containers to the vaporizer and preheater, respectively. The nonreturn valves were used at the feed inlets to restrict the back flow of the hot reaction mass. Both solvents were vaporized in the preheater-vaporizer, and

the vapor mixture flowed into the PPFR where the steam cracking of TODGA was carried out over a temperature range of 550 to 1100 °C. The flow rate of TODGA and water to TODGA mol ratio were varied from 5.6 to 28.8 g h^{-1} and 0 to 208, respectively, at the different temperatures. The reaction products were condensed in the condenser system and, finally, separated into liquid and gaseous products in a phase separator. The gaseous products were sent to a digital gas flow meter and then collected for analysis by gas chromatography. The liquid products were analyzed separately by gas–liquid chromatography.

2.3. Analytical Methods. The quantitative analysis of all the gaseous products was conducted using a Thermo Scientific Gas Chromatograph 8610 C, equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The hydrocarbon gases (C_2–C_4) such as acetylene, ethylene, ethane, 1-propene, n-propane, 1-butene, and n-butane were identified and quantified by GC-FID on a Hayesep D stainless steel packed column (25 feet in length, ID 2.4 mm). Nitrogen was used as a carrier gas with a flow rate of 20 cm^3/ min. The oven temperature and FID's temperature were held constant at 120 and 250 °C, respectively. Injector port's temperature was maintained at 80 °C. In the GC-TCD method, nitrogen was used as a carrier to detect H_2, O_2, CO, and CH_4, whereas hydrogen was used as a carrier gas to analyze N_2 and CO_2. The oven, injector, and TCD's temperatures were maintained at 25 °C, 30 °C, and 100 °C, respectively. The flow rates of nitrogen and hydrogen were adjusted at 15 cm^3/ min.

The aqueous liquid phase was equilibrated with benzene to extract the liquid products, and the organic extract was analyzed by using the GC-FID method. A 10% OV-17 SS packed column (4 m in length, ID 2.4 mm) was used for the separation of the liquid components. Nitrogen was used as carrier gas with a flow rate of 20 cm^3/min. The GC was programmed for a temperature gradient with initial temperature of oven held at 150 °C for 6 min, followed by a heating rate of 10 °C/min up to 250 °C, held at there for 2 min and then followed by another heating rate of 10 °C/min up to 340 °C, where it was held for 10 min. The temperature of the injector port and FID was maintained constant at 340 and 350 °C, respectively. In the liquid phase, n-octyl amine, di-n-octyl amine, and unconverted TODGA were identified and quantified as the major products. All the gaseous and liquid products were identified by comparing their retention indices with those of standard components.

3.0. RESULTS AND DISCUSSION

3.1. Effect of Temperature. The effect of temperature on the conversion of TODGA and on overall product's composition was studied experimentally in the range of 550 to 1100 °C. The flow rate of TODGA was kept constant at 5.6 g h^{-1}, whereas the flow rate of distilled water was maintained at 36 g h^{-1}. The water to TODGA mol ratio was maintained at 208 for thermal decomposition of TODGA. The effect of temperature on conversion and the overall gaseous and liquid products yields is shown in Figure 3. As expected, the conversion of TODGA increased from 42 to 100 wt % with the temperature increasing from 550 to 1100 °C. The volume of product gases increased from 6.6 to 100 wt %, whereas a collective volume of the liquid products decreased from 93 to 0 wt % with the increasing temperature. At 1050 °C, complete gasification of TODGA was observed in the given reactor. No
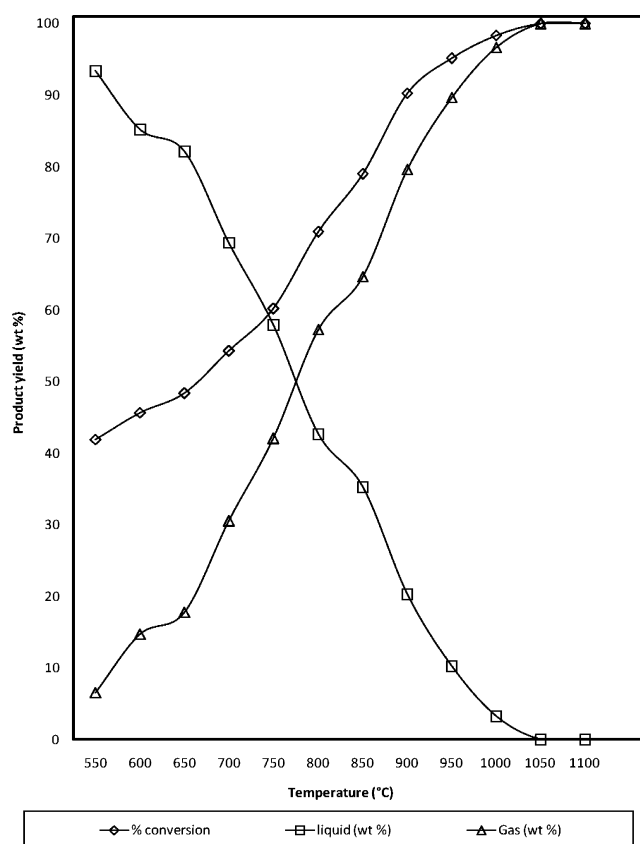

Figure 3. Effect of temperature on overall product's yield during the steam pyrolysis of TODGA, (flow rate of TODGA = 5.6 g h^{-1}, water to TODGA mol ratio = 124).

coke or char formation took place in these experiments as the superheated steam was used in a large excess.

In the liquid products, mainly unreacted TODGA, di-n-octyl amine, and n-octyl amine were characterized and quantified. In the gaseous products, the presence of H_2, O_2, N_2, CO, CO_2, CH_4, acetylene, ethylene, ethane, 1-propene, n-propane, 1-butene, and n-butane were detected. The complete qualitative and quantitative analysis of all the liquid and gaseous products distribution is schematically shown in Figure 4(A),(B). Figure 4(A) shows that the yield of dioctyl amine and unconverted TODGA decreased from 10.4 to 0 and 11 to 0 mol %, as they further decomposed into N_2 and hydrocarbon gases (C_1–C_4). Another liquid product octyl amine also decreased in yield from 9.2 to 0 mol % with increasing the temperature from 550 to 1000 °C (Figure 4(B)). Among the gaseous products, H_2 was produced in the highest yield, followed by CO_2 and CH_4. The yield of H_2 increased from 34 to 52 mol % with the increasing temperature, which indicates that the dehydrogenation of organic components are taking place extensively over the metallic surface of SS 316 flow reactor. CH_4 and N_2 have shown significant increasing yield from 6.4 to 12.5 mol % and 5 to 9.4 mol %, respectively. The mol % of O_2 (7.5 to 4.3) and CO (7.3 to 3.1) decreased, whereas the yield of CO_2 (7 to 13 mol %) increased continuously, indicating the oxidation reactions are taking place in the steel reactor. However, the formation of hydrocarbon gases (C_2–C_4) was very low in the yields (Figure 4(B)). All the hydrocarbon gases show a slightly increasing trend with the increasing temperature. Among the C_2–C_4 gases, ethylene (0.6 to 1.9 mol %) and ethane (0.35 to 1 mol %) were produced in slightly higher amounts, whereas 1-
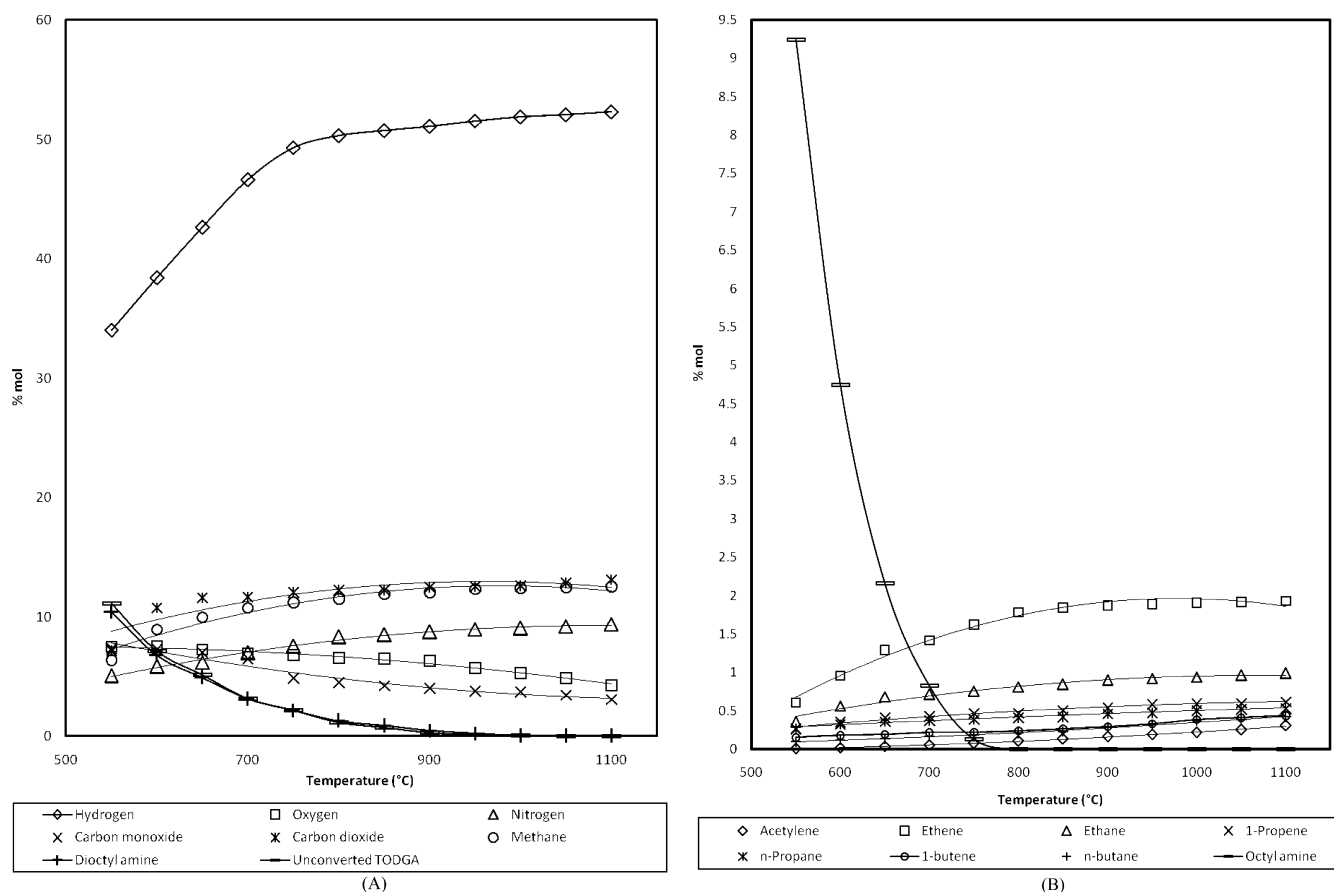
Figure 4. A. Effect of temperature on the yield of H_2, O_2, N_2, CO, CO_2, CH_4, dioctyl amine, and unconverted TODGA (mol %) in the steam pyrolysis of TODGA (mol of product formed/100 mol of TODGA decomposed); flow rate of TODGA = 5.6 g h^{-1}, water to TODGA mol ratio = 208. B. Effect of temperature on the yield of hydrocarbon gases (C_2–C_4) and octyl amine (mol %) in the steam pyrolysis of TODGA (mol of product formed/100 mol of TODGA decomposed); flow rate of TODGA = 5.6 g h^{-1}, water to TODGA mol ratio = 208.

propene, *n*-propane, 1-butene, and *n*-butane were produced in very low yield (<0.8 mol %). Overall, it was observed that with the increasing temperature and in the presence of superheated steam, the heavier organic product components (C_1–C_8) are completely broken down into H_2, CO, CO_2, N_2, and CH_4 as the major products.

3.2. Effect of Water to TODGA Mol Ratio. The effect of water to TODGA mol ratio (0 to 208) was investigated on the conversion of TODGA, overall products distribution, and, particularly, on the formation of char to estimate the optimized process variables at which pyrolysis of TODGA can be carried out without the coke formation. In the absence of steam at 800 °C, the char yield was found 4.3 wt %, whereas at 1000 °C, the char yield was 12 wt % (Figure 5). At higher water to TODGA mol ratio (i.e., more than 175), no char formation was observed in the temperature range of 800 to 1000 °C. From these observations, it is confirmed that the coke formation mainly depends on temperature and the steam to organic feed ratio. Thus, in a metallic SS flow reactor, use of a large excess of steam is advisable to avoid the coke formation at the higher temperature range. It has been observed that steam reacts with high molecular weight and high boiling organic components and oxidizes them into their oxides, which restricts the formation of coke during the pyrolysis process. At the higher steam to TODGA mol ratio, the formation of H_2, CO, and CO_2 was observed in high yields. This is due to the dehydrogenation reactions of hydrocarbons occurring in the reactor, producing

carbene or methylene radicals. Further, steam reacts with carbene to form CO and H_2, resulting in the coke inhibition. CO further undergoes water-gas shift reaction to generate CO_2. In steam cracking reaction of petroleum refinery operations, the selective solid catalysts are commonly employed to minimize the coke formation and, also, to increase the yield of specific value-added products. In this work, the use of solid catalyst is avoided purposely, as at the nuclear industrial plants, there will be a risk of transferring the radioactivity from the radioactive waste solvents to the solid catalyst, which may further lead to the secondary solid waste deposition problems.

Figure 6 shows the effect of water to TODGA mol ratio on conversion and overall product yield at 1000 °C. The conversion of TODGA increased from 55.5 to 98 wt % and total gas yield increased from 29 to 98 wt %; with the increasing amount of steam that confirms the enhancement in the bond breaking by superheated steam, followed by the complete gasification of TODGA. The yields of all the liquid products and coke decreased from 59 to 1.6 wt % and 12 to 0 wt %, respectively, with increasing the water to TODGA mol ratio. It is confirmed that steam thus not only inhibits the coke formation but also intensifies the gasification process by enhancing the breaking of chemical bonds in the organic components.

The effect of water to TODGA mol ratio on overall products distribution at 1000 °C is shown schematically in Figure 7(A), (B). The yield of CO and CO_2 increased from 0.8 to 3.3 mol %
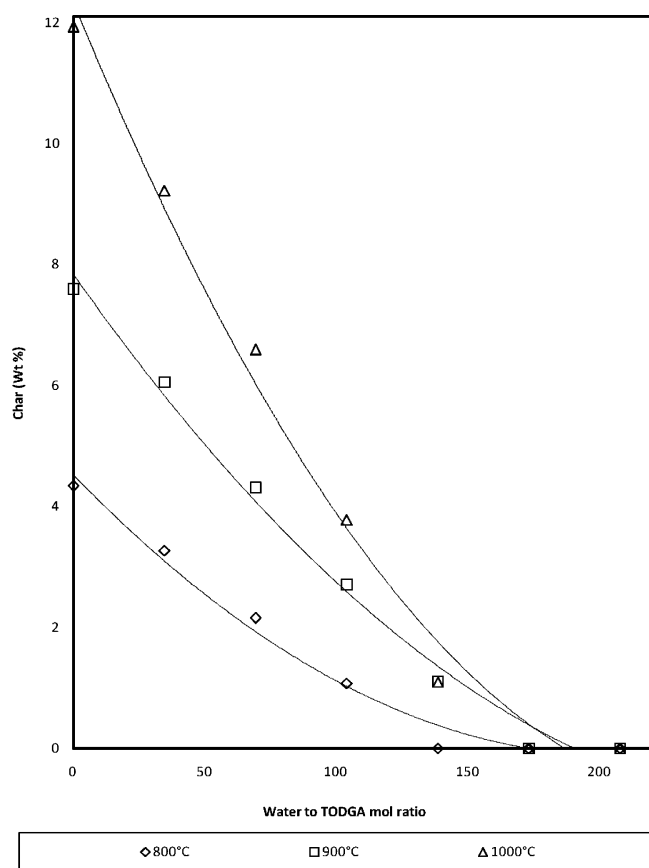
Figure 5. Effect of water to TODGA mol ratio on formation of char at different temperatures, flow rate of TODGA = 5.6 g h^{-1}.

Figure 6. Effect of water to TODGA mol ratio on overall products yield at 1000 °C, flow rate of TODGA = 5.6 g h^{-1}.

and 12.5 to 21 mol %, respectively with the increasing amount of steam. The amount of O_2 (3.2 to 6.8) and N_2 (3.1 to 7.5) also increased with increasing water to TODGA mol ratio. There is a prominent reduction in the yield of dioctyl amine (3.2 to 0 mol %) and no octyl amine was formed in the liquid products. The noticeable increase in the yield of H_2 (45.9 to 51.7 mol %) was observed with increasing amount of steam. Almost, all hydrocarbon gases (C_2–C_4) show the decreasing trend with increasing steam to feed ratio. Figure 7(B) shows that the total yield of all hydrocarbon gases is low (<6 mol %) compared to CO, CO_2, CH_4, and other permanent gases. Among the C_2–C_4 gases, the highest yield products were ethylene (1.8 to 4.3 mol %) and ethane (0.9 to 2.6 mol %). The yield of acetylene reduced from 1.3 to 0.1 mol % with increasing the amount of steam. It was also observed that as compared to the alkane gases (viz. ethane, *n*-propane, and *n*-butane), the olefinic gases (viz. ethylene, 1-propene, and 1-butene) are produced in slightly higher yields, which is probably due to the dehydrogenation of the saturated hydrocarbon gases. A catalytic reaction on the metal surface, in the presence of steam, is not ruled out.

3.3. Effect of Flow Rate and Residence Time. The effect of TODGA's flow rate on the conversion was studied in the range of 5.6 to 28 g h^{-1} at temperatures 850, 900, 950, and 1000 °C with the fixed water to TODGA mol ratio (i.e., 208). With increasing flow rate, the residence time obtained for the feed in a tubular PPFR decreased, resulting in the lower conversion of TODGA. It was observed that the conversion of TODGA decreased with the increasing flow rate (Figure 8). The highest conversion of TODGA (98.4 wt %) was noticed at
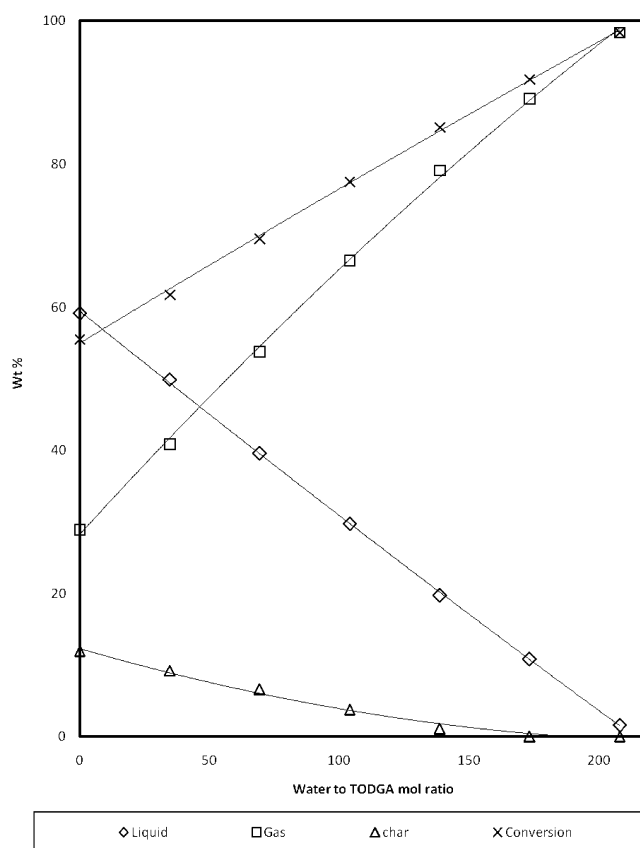
1000 °C with the flow rate of 5.6 g h^{-1}, whereas the lowest conversion (32.8 wt %) was observed at 850 °C with a flow rate at 28 g h^{-1}. Considering the vaporization and change in the number of moles of reacting components, the average residence time calculated for the cracking of TODGA in a PPFR was about 0.18 to 1 s. The effect of residence time on the overall products composition during the steam pyrolysis of TODGA at 850 °C is shown in Figure 9(A),(B). Figure 9(A) shows that H_2 is the major product, which further increased (39.8 to 44 mol %), with increasing residence time from 0.2 to 1 s. The yield of dioctyl amine reduced from 8.8 to 1.4 mol % with the increasing residence time. The yields of N_2 (7.8 to 10 mol %), CH_4 (3 to 3.5 mol %), and CO (4 to 5.7 mol %) slightly increased with the residence time. Also, the O_2 and CO_2 have shown significant increments in their yields from 5.9 to 6.9 and 7.6 to 9.2 mol %, respectively. Figure 9(B) shows a feebly increasing trend in the yield of almost all the hydrocarbon gases (C_2–C_4) with increasing residence time. Among the hydrocarbon gases, ethylene (10 to 11.5 mol %), 1-propene (0.3 to 3.9 mol %), and ethane (0.1 to 1.7 mol %) were generated in slightly higher yields, whereas acetylene (0.07–0.12 mol %), *n*-propane (0.01–0.16 mol %), 1-butene (0.07–0.9 mol %), and *n*-butane (0.01–0.03 mol %) were produced in negligible amounts (Figure 9(B)).

From the experimental observations, the optimized process variables for the complete gasification of TODGA, without the coke formation, are estimated at reactor temperature of 1050 °C, water to TODGA mol ratio of 175, and TODGA's flow rate at 5.6 g h^{-1} in the used PPFR by using a "one-factor-at-a-time-approach", in which one factor is varied manually, while others
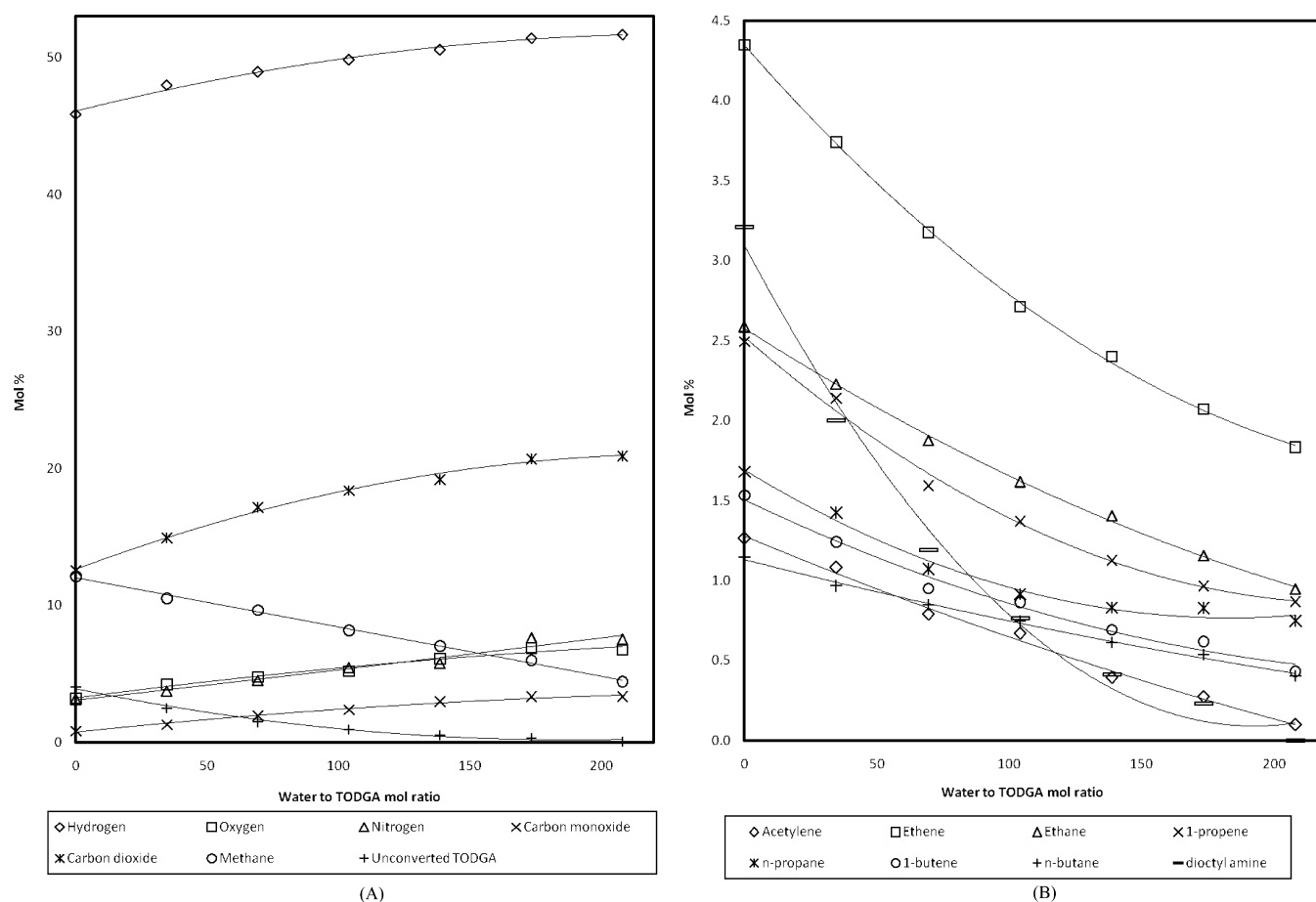
Figure 7. A. Effect of water to TODGA mol ratio on the yield of H_2, O_2, N_2, CO, CO_2, CH_4, and unconverted TODGA (mol %) at 1000 °C, flow rate of TODGA = 5.6 g h^{-1}. B. Effect of water to TODGA mol ratio on the yield of acetylene, ethylene, ethane, 1-propene, n-propane, 1-butene, n-butane, and dioctyl amine (mol %) at 1000 °C, flow rate of TODGA = 5.6 g h^{-1}.

are kept at constant level and the optimization of the process is carried out.

3.4. Kinetics of Steam Pyrolysis of TODGA. Steam pyrolysis of TODGA (A_F) is assumed to be an irreversible, first-order reaction governed by the following relation

$$A_F + S_W \rightarrow \text{products} \tag{1}$$

Since, steam (S_W) is used in large excess in a tubular plug flow reactor, the following kinetic model is considered to represent the pseudo-first-order, irreversible pyrolysis reaction[48−50]

$$\kappa \cdot \tau = (1 + \varepsilon)\ln(1/1 - X) - \varepsilon \cdot X \tag{2}$$

The conversion of TODGA to the reaction products mainly depends upon the temperature and residence time as shown in Figure 10. The moles of products formed per mole of TODGA pyrolyzed, τ (residence time), X (conversion of TODGA), and ε (relative change of volume of reaction mass in the system, when passing from zero to total conversion), were determined, experimentally. The right-hand term of eq 2, as a function of the residence time (τ) at given temperatures, is schematically shown in Figure 11. The estimated apparent values of the rate constants (k) are given in Table 1. These values of rate constants adequately represent the rate of steam pyrolysis of TODGA as a pseudo-first-order reaction. There is no self-inhibition effect of the pyrolysis products due to the presence of a large excess of steam. Steam not only reduces the partial pressure of the reacting components but also continuously

converts the heavy precursors of coke into CO, CO_2, and H_2. Consequently, steam minimizes the secondary reaction pathways and restricts the formation of coke. The approximate activation energy of the steam pyrolysis of TODGA in the temperature range of 850−1000 °C was estimated to be 123 kJ/mol.

3.4.1. Reaction Network Model. The overall theoretical scheme for the steam pyrolysis of TODGA assumed is as follows:

$$\underset{\text{TODGA}}{C_{36}H_{72}O_3N_2} + \underset{\text{Steam}}{69H_2O} \rightarrow 36CO_2 + 105H_2 + N_2 \tag{3}$$
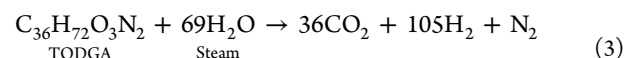
But, the meticulous analysis of all the reaction products confirms that the reaction network model of the steam thermolysis of TODGA is not as simple as the assumed theoretical scheme, shown in eq 3. On the basis of a detailed qualitative and quantitative analyses of all the reaction products (i.e., 13 gases and 3 liquid components) and also, by assuming the formation of some highly unstable reaction intermediates in the PPFR, a comprehensive reaction mechanism of the steam pyrolysis of TODGA is proposed below.

TODGA is having three weak bonds i.e. amide ($-CO-NR_1R_2$), ether ($-CH_2-O-CH_2-$), and the bond adjacent to amidic linkage ($-CH_2-CO-$),[42] which can undergo thermal cracking, straightforwardly. Hence, three initiation reactions are possible in the steam pyrolysis of TODGA. In reaction 4, dioctyl amine (DOA) and N,N-dioctyl diglycolamide (DODGA) are formed due to breaking of the amide bonds,
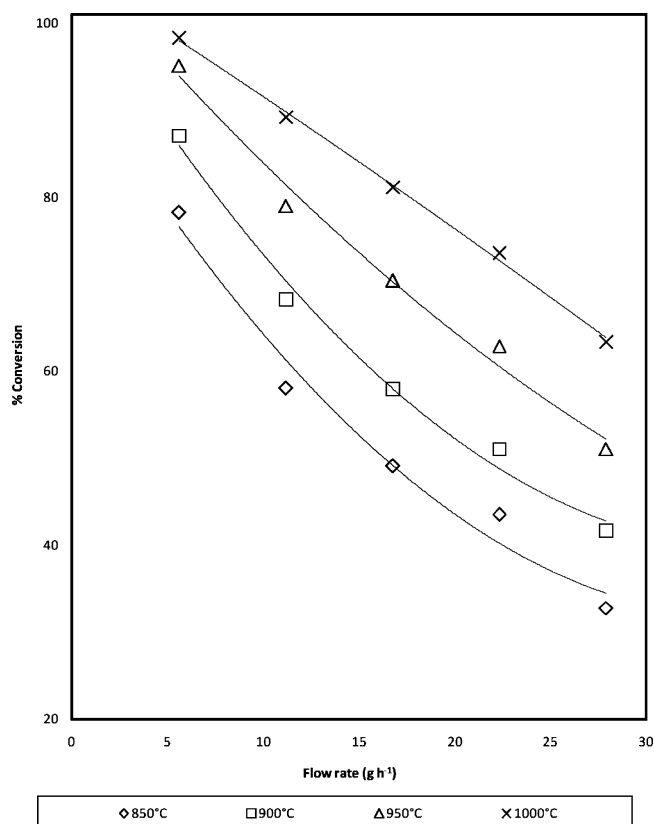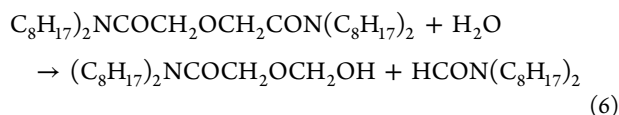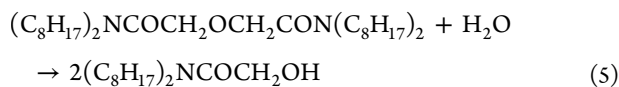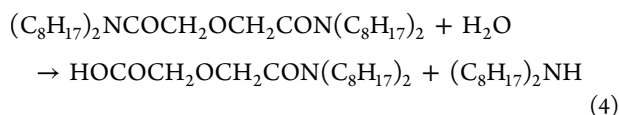
Figure 8. Effect of flow rate on conversion of TODGA at different temperatures; water to TODGA mol ratio = 208.

whereas in reaction 5, two moles of N,N-dioctyl glycolamide (DOGA) are produced as a result of symmetrical disintegration of the ether bonds of TODGA. Further, reaction 6 shows the cleavage of the bond adjacent to the amide linkage resulting in the formation of N,N-dioctyl methylene hydroxide glycolamide intermediate and N,N-dioctyl formamide (DOFA).

$$(C_8H_{17})_2NCOCH_2OCH_2CON(C_8H_{17})_2 + H_2O$$
$$\rightarrow HOCOCH_2OCH_2CON(C_8H_{17})_2 + (C_8H_{17})_2NH \quad (4)$$

$$(C_8H_{17})_2NCOCH_2OCH_2CON(C_8H_{17})_2 + H_2O$$
$$\rightarrow 2(C_8H_{17})_2NCOCH_2OH \quad (5)$$

$$C_8H_{17})_2NCOCH_2OCH_2CON(C_8H_{17})_2 + H_2O$$
$$\rightarrow (C_8H_{17})_2NCOCH_2OCH_2OH + HCON(C_8H_{17})_2 \quad (6)$$

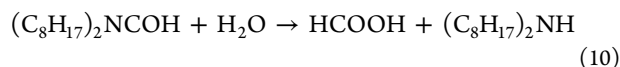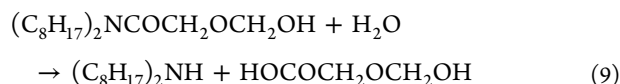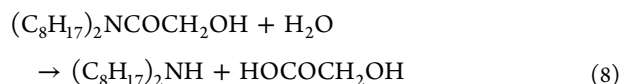All these high molecular weight intermediates further undergo thermal cracking. In reaction 7, the N,N-dioctyl diglycolamide further breaks down into diglycolic acid and dioctyl amine.
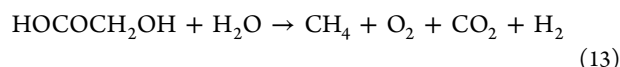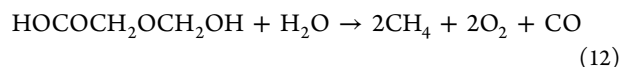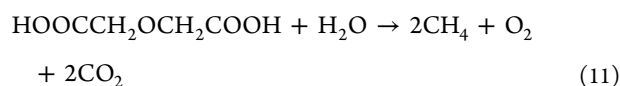
$$HOCOCH_2OCH_2CON(C_8H_{17})_2 + H_2O$$
$$\rightarrow HOCOCH_2OCH_2COOH + (C_8H_{17})_2NH \quad (7)$$
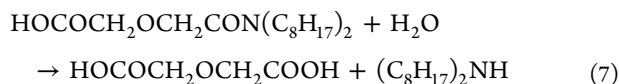
Reaction 8 shows fragmentation of DOGA into dioctyl amine and α-hydroxy acetic acid. Further, reaction 9 indicates the decomposition of N,N-dioctyl methylene hydroxide glycolamide intermediate into dioctyl amine and α-hydroxy glycolic
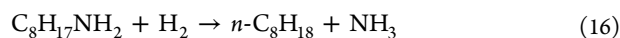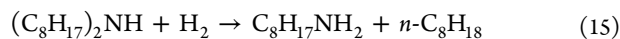
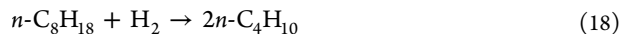acid. In reaction 10, dioctyl formamide (DOFA) is further hydrolyzed into formic acid and dioctyl amine.

$$(C_8H_{17})_2NCOCH_2OH + H_2O$$
$$\rightarrow (C_8H_{17})_2NH + HOCOCH_2OH \quad (8)$$

$$(C_8H_{17})_2NCOCH_2OCH_2OH + H_2O$$
$$\rightarrow (C_8H_{17})_2NH + HOCOCH_2OCH_2OH \quad (9)$$

$$(C_8H_{17})_2NCOH + H_2O \rightarrow HCOOH + (C_8H_{17})_2NH \quad (10)$$

In reactions 11 and eq 12, diglycolic acid and α-hydroxy glycolic acid further decomposed to CH_4, O_2, CO_2, and CO, respectively. In reaction 13, α-hydroxy acetic acid further pyrolyzed in CH_4, O_2, CO_2, and H_2. In reaction 14, formic acid undergoes C−O cleavage to form carbon dioxide and hydrogen.

$$HOOCCH_2OCH_2COOH + H_2O \rightarrow 2CH_4 + O_2$$
$$+ 2CO_2 \quad (11)$$

$$HOCOCH_2OCH_2OH + H_2O \rightarrow 2CH_4 + 2O_2 + CO \quad (12)$$

$$HOCOCH_2OH + H_2O \rightarrow CH_4 + O_2 + CO_2 + H_2 \quad (13)$$

$$HCOOH \rightarrow CO_2 + H_2 \quad (14)$$

In reaction 15, dioctyl amine (DOA) hydrogenates to produce n-octyl amine and n-octane. Further, in reaction 16, n-octyl amine reacts with H_2 to produce ammonia and n-octane. Ammonia is completely decomposed into N_2 and H_2 (reaction 17) as proved by its absence in the products.

$$(C_8H_{17})_2NH + H_2 \rightarrow C_8H_{17}NH_2 + n\text{-}C_8H_{18} \quad (15)$$

$$C_8H_{17}NH_2 + H_2 \rightarrow n\text{-}C_8H_{18} + NH_3 \quad (16)$$

$$2NH_3 \rightarrow N_2 + 3H_2 \quad (17)$$

In reactions 18−27, n-octane undergoes a series of thermal cracking reactions to form C_1−C_4 gases such as CH_4, acetylene, ethene, ethane, 1-propene, n-propane, 1-butene, and n-butane.[54]

$$n\text{-}C_8H_{18} + H_2 \rightarrow 2n\text{-}C_4H_{10} \quad (18)$$

$$n\text{-}C_4H_{10} \rightarrow 1\text{-}C_4H_8 + H_2 \quad (19)$$

$$n\text{-}C_4H_{10} \rightarrow 1\text{-}C_3H_6 + CH_4 \quad (20)$$

$$n\text{-}C_4H_{10} \rightarrow C_2H_4 + C_2H_6 \quad (21)$$

$$n\text{-}C_4H_{10} \rightarrow 2C_2H_4 + H_2 \quad (22)$$

$$1\text{-}C_3H_6 \rightarrow C_2H_2 + CH_4 \quad (23)$$

$$C_2H_6 \rightarrow C_2H_4 + H_2 \quad (24)$$

$$1\text{-}C_3H_6 + H_2 \rightarrow n\text{-}C_3H_8 \quad (25)$$

$$2C_2H_6 \rightarrow n\text{-}C_3H_8 + CH_4 \quad (26)$$

$$n\text{-}C_3H_8 \rightarrow C_2H_4 + CH_4 \quad (27)$$

In the secondary reactions, methane undergoes oxidative hydrolysis with steam to form CO and hydrogen (reaction

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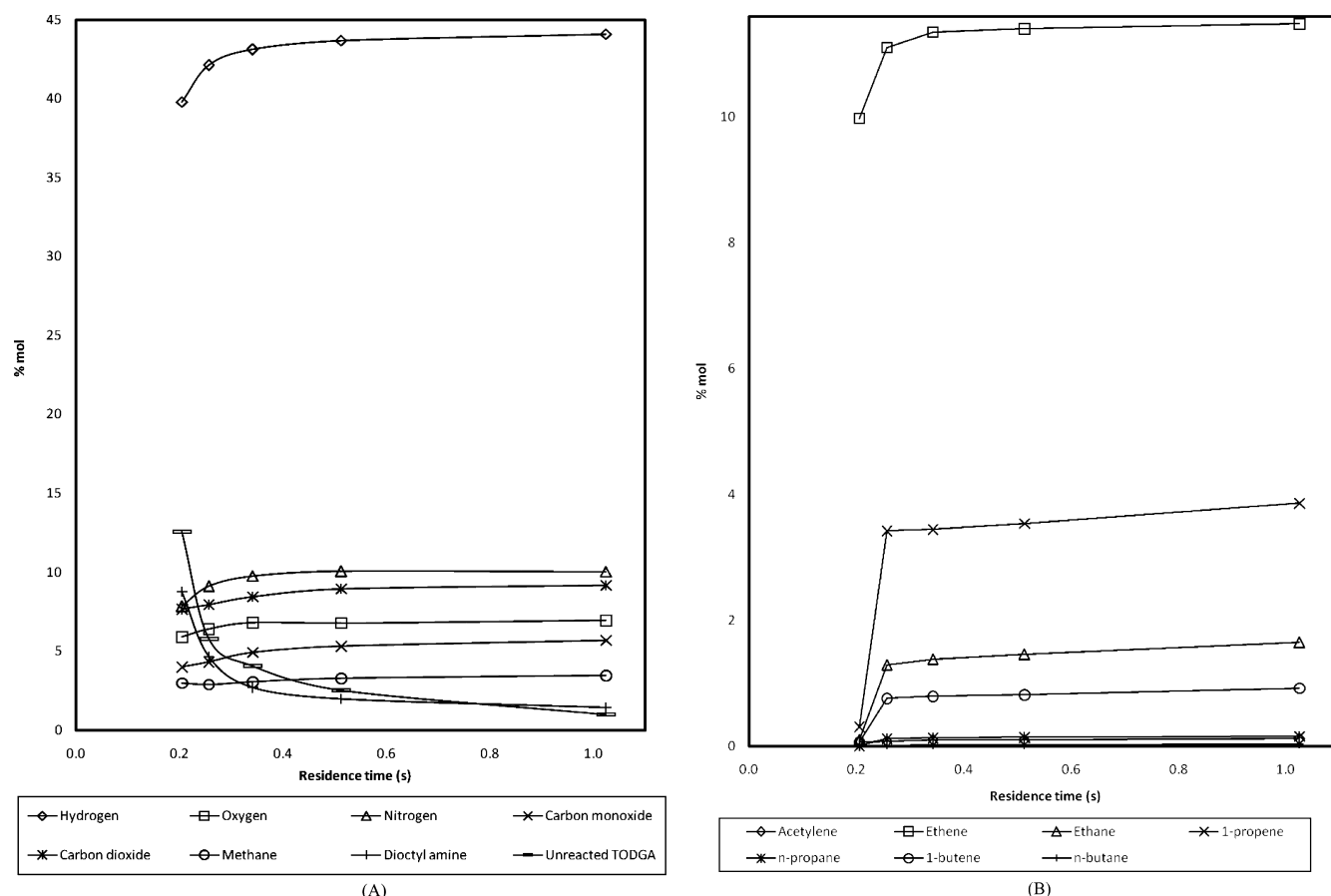dx.doi.org/10.1021/ie302603q | *Ind. Eng. Chem. Res.* 2013, 52, 2457−2469

Figure 9. A. Effect of residence time on the yield of H_2, O_2, N_2, CO, CO_2, CH_4, dioctyl amine, and unconverted TODGA (mol %) at temperature of 850 °C, water to TODGA mol ratio = 208. B. Effect of residence time on the yield of acetylene, ethylene, ethane, 1-propene, n-propane, 1-butene, and n-butane (mol %) at temperature of 850 °C, water to TODGA mol ratio = 208.

28). In reaction 29, carbon monoxide further undergoes waste-gas shift reaction to form carbon dioxide and hydrogen.[49]

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (28)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (29)$$
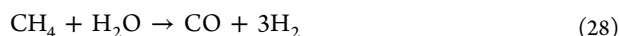
In the absence of steam, the methane and saturated hydrocarbons (e.g., C_2–C_4) may undergo charring to form coke and hydrogen as shown in reaction 30.

$$CH_4 \rightarrow C + 2H_2 \qquad (30)$$

Steam converts the coke and char particles into carbon monoxide, carbon dioxide, and hydrogen, probably on the catalytic surface of the reactor as shown in reactions 31 and 32.

$$C + H_2O \rightarrow CO + H_2 \qquad (31)$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 \qquad (32)$$
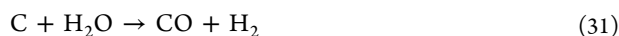
The proposed reaction network model can be useful in developing the detailed mathematical kinetic model of the steam pyrolysis of TODGA. Estimation of the kinetic parameters of this reaction mechanism is now the subject of further investigations.

3.5. Investigation of the Possibility of Runaway Reactions of TODGA-HNO₃ Mixtures. At elevated temperatures (>130 °C), thermal decomposition of TBP-HNO₃-heavy metal nitrate mixtures (i.e., red oil) in the closed evaporators results in the explosive runaway reactions.[22] The runaway accidents are potentially very hazardous and cause a big setback

at nuclear reprocessing plants, e.g. red oil explosion at Tomsk-7 in 1993 and at Savannah River in 1953. Thus, it is very important to mention here the complete product's profile of the red oil decomposition found during the TBP-HNO₃ runaway explosions which took place at several nuclear reprocessing plants worldwide. We also report here the products composition obtained in the lab-scale experiments of red oil degradation performed by us, at atmospheric pressure. In the incidents at Savannah River (1953) and Hanford (1953), butyric acid was identified.[55] Liquid butyl nitrate, butyl nitrite, and gaseous 1-butene were identified as the products of thermal decomposition of nitrated TBP in the presence of heavy metals.[56−60] In the Tomsk-7 (1993) incident methane was observed, which was probably due to the thermal decomposition of hydrocarbon diluent i.e. n-dodecane. Butyric acid, butyl nitrate, and 1-butene are genetically related compounds in thermal decomposition of TBP. Butyl nitrate and butyl nitrite are also formed by exothermic dealkylation of TBP in the presence of nitrates.[56,57] 1-Butene is formed by endothermic decomposition (i.e., pyrolysis) of TBP under conditions of deficient or lacking nitrates and at higher temperatures as compared to the typical dealkylation temperatures. Also, 1-butene is formed by the decomposition of butyl nitrate at temperatures, somewhat higher than the boiling point of butyl nitrate (136 °C). In the explosions, both butyl nitrate and 1-butene are oxidized into butyric acid. For butyl nitrate and butyric acid, the lower explosive limits in air are 1.5 and 2.1
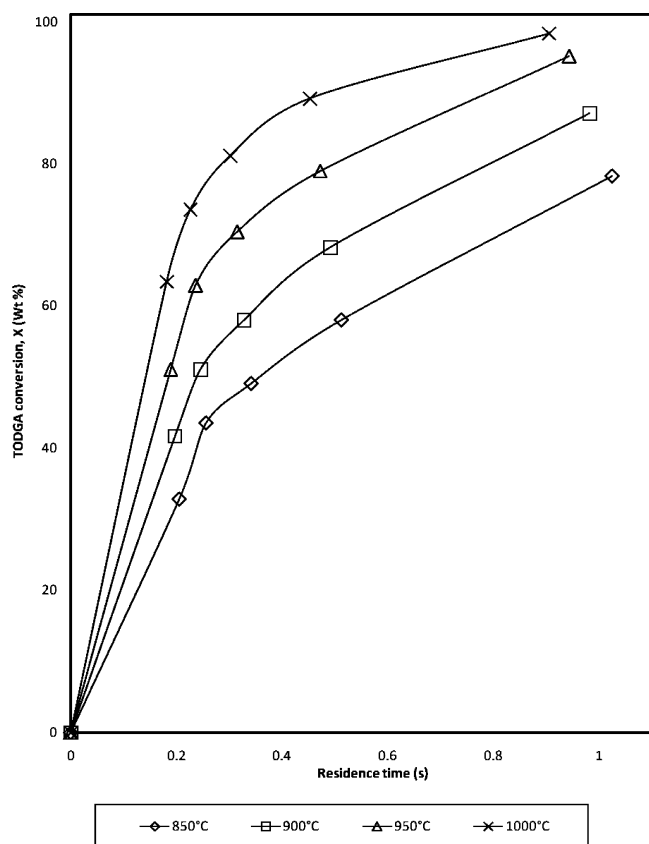
Figure 10. Conversion of TODGA as a function of residence time at various temperatures.

Figure 11. Graphical presentation of eq 2 for pseudo-first-order, irreversible reaction of steam pyrolysis of TODGA at different temperatures.

vol %, respectively.[58] Also, the air containing 1.7 to 9 vol % of 1-butene is dangerously explosive.[61]

From the analysis of literature, experimental studies of red oil decomposition, and the careful analysis of products, at present, it is a very well-understood fact that the presence of organic nitrates, nitrites, acids, alcohols, and flammable hydrocarbon gases (C_1–C_4) are the main culprits of the explosive runaway reactions.[20,59] Butanol vigorously reacts with nitric acid to form butyl nitrate, which further quickly decomposes even at room temperature and results in highly exothermic and explosive reactions. Formation of NO, NO_2, and N_2O is the obvious indication of such explosive reactions.

Toward the end of the solvent extraction processes such as DIAMEX and SANEX, some amount of TODGA may remain entrained or suspended in the waste aqueous nitric acid phase containing heavy metal nitrates, which is a threatening factor from the runaway explosions point of view. Consequently, before the industrial appliance of TODGA as a nuclear extractant, it becomes very important to understand its nitration phenomenon with red oil formation, its complete product's profile during the nitrolysis, and its possible reaction mechanism to predict the possibility of runaway reactions and to set the relevant control measures.

Thus, a few experiments were conducted in the given PPFR to study the thermal decomposition of TODGA in the presence of 4 M HNO_3 and air/O_2 (here, air was not evacuated from the pyrolysis setup during the experimentations). The experimental data were obtained in a temperature range of 130–400 °C at overall atmospheric pressure. On the basis of GC-TCD-FID and mass spectroscopic analysis, it was observed that the gaseous products formed in the steam nitrolysis of TODGA
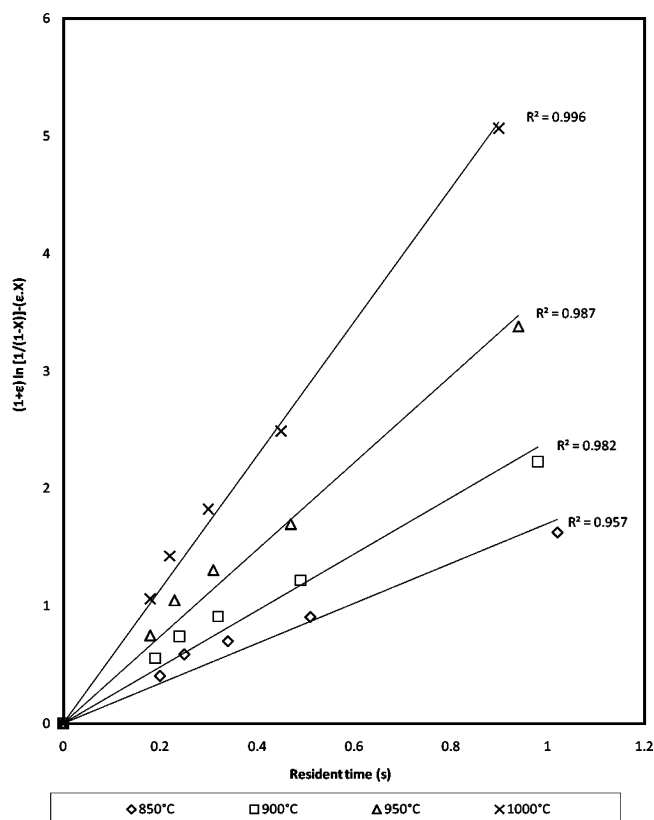
Table 1. Rate Constants (k) for the Steam Pyrolysis of TODGA

temp (K)	rate constant k (exp.), s^{-1}
1123	1.18
1173	2.28
1223	3.67
1273	5.62

were as similar to the products formed during the thermal decomposition of TBP-HNO_3/red oil mixtures. In the steam nitrolysis of TODGA, the gaseous products produced were H_2, N_2, O_2, CO, CO_2, CH_4, NO, N_2O, acetylene, ethene, ethane, 1-propene, n-propane, 1-butene, and n-butane. No appreciable amount of NO_2 was present in the final product mixture, although an orange color was observed, suggesting the presence of NO_2 in the early stages of thermal decomposition. The liquid products of the steam nitrolysis of TODGA were separately analyzed by using Shimadzu Gas Chromatograph QP 2010 plus, incorporated with a single quadruple mass analyzer that was operated in electron ionization (EI) mode. A capillary column DB 624 (60 m length, 0.32 mm OD, 1.8 μm film thickness) engaged with a Shimadzu Gas Chromatograph was equilibrated with helium as a carrier gas.

On the basis of the GC-MS analysis of the products, it was clearly observed that the butyl nitrate and butyl nitrite were not produced during the steam nitrolysis of TODGA, which are the principal components of the explosive TBP-HNO_3 red oil. It was also observed that butanol, buteraldehyde, and C_1–C_4 carboxylic acids were not formed in the steam nitrolysis of TODGA, which are also the major components of "red oil" and

the main perpetrators of the runaway explosions. Certainly, it can be estimated that the formation of NOx gases is due to the decomposition of nitric acid only and not because of the destruction of butyl nitrate or butyl nitrite. The flammable gases like 1-butene, *n*-butane, and acetylene were observed in the steam nitrolysis of TODGA, but their volume is far lower than their explosive limits (<1.7−9 vol %). Thus, on the basis of experimental results and detailed analysis of reaction products, the initial presumption can be made that the possibility of explosive runaway reactions during the steam nitrolysis of TODGA is rare using the type of facilities, pyrolysis reactor, and the reaction conditions used in this study. Also, TODGA has negligible solubility in the aqueous nitric acid phase (i.e., 24.3 ppm), compared to TBP (400 ppm).[60,61] Thus, at the end of the DIAMEX and SANEX processes, a significantly less quantity of TODGA may remain in the waste acidic raffinate, which is lower than the explosive limits and, probably, cannot cause runaway reactions. This useful evidence can sustain the industrial employment of TODGA as the safe nuclear extractant instead of TBP at nuclear reprocessing plants.

3.6. Treatment of Harmful Products. Among all the reaction products of steam pyrolysis of TODGA, H_2, N_2, CH_4, CO, and CO_2 are the high yield gases, whereas the yield of hydrocarbon (C_1-C_4) gases is very low (<3 mol %). The C_1-C_4 hydrocarbon gases, H_2, CO, and NOx produced during the steam pyrolysis and nitrolysis of TODGA are still hazardous pollutants, and direct emission of these toxic gases to the environment may not be a safe practice. Also, the hydrocarbon gases such as acetylene, ethene, propene, butane, and butane are highly flammable. The presence of a huge amount of H_2 along with C_2-C_4 hydrocarbon gases at industrial pyrolysis plants is highly unsafe and may lead to accidents. Hence, all the toxic and flammable gases must be treated properly. The "three way-catalytic conversions" is a very popular technology used in modern automobiles, which mainly consists of the catalytic active materials viz. alumina oxide, cerium oxide, rare earth stabilizers, platinum, palladium, and rhodium. The function of a three-way catalytic converter is to transform the hazardous and flammable gases like H_2, C_1-C_4 hydrocarbons, CO, and NOx completely into safe and nontoxic species such as H_2O, CO_2, and N_2, on the catalytic active surface at 300−350 °C.[62,63]

The eco-friendly and stable components can be released to the atmosphere after passing through the "high efficiency particulate (HEPA) filter bank" to remove the trace amount of radio nuclides (up to 0.3 μm particle size) that can avoid their lethal effect on the environment and living organisms. HEPA filters are mainly used to filter out highly hazardous aerosols that are radioactive and highly lethal.[64]

CONCLUSION

The steam pyrolysis process can be efficiently employed for the complete thermal decomposition and gasification of amide based waste extractants at overall atmospheric pressure. A continuous steam pyrolysis of TODGA in a SS 316 plug flow reactor over a temperature range of 850 to 1000 °C is found to be an irreversible, pseudo-first-order reaction with approximate activation energy of 123 kJ/mol. The presence of high excess of superheated steam, which reacts with the precursors of coke over the catalytic surface of the reactor, inhibits the further coke formation. The conversion of TODGA and overall product's composition at the given reaction conditions mainly depend upon the temperature, steam to feed ratio, and residence time.

The coke formation can be avoided by optimizing the conditions of temperature and water to organic feed ratio. Steam is an efficient coke inhibitor, diluent, carrier, and pyrolyzing media in the flow reactors. At 1050 °C, TODGA's flow of 5.6 g h^{-1} and at water to TODGA mol ratio of 180, the complete gasification of TODGA was observed without the coke formation.

The products of steam nitrolysis of TODGA are non-explosive and innocuous in nature. Consequently; the possibility of runaway accidents during the nitration of TODGA is very rare. This experimental data and process could be the useful asset for the industrial scale up of thermal decomposition of low level waste radioactive diglycolamides, malonamides, and other organic solvents even in the presence of nitric acid.

ASSOCIATED CONTENT

⑤ Supporting Information

Figures S1−S10 show the mass, ^{1}H-NMR, and FTIR spectrum of intermediates and final product in support of the claimed structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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