



# Modeling and optimizing of steam pyrolysis of dimethyl formamide by using response surface methodology coupled with Box-Behnken design

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## ABSTRACT

A non-catalytic steam pyrolysis of N,N-dimethyl formamide (DMF) was studied in a SS 316 plug flow reactor at atmospheric pressure as a waste solvent minimization method. The reaction products were analyzed by using gas chromatography-thermal conductivity detector and high performance liquid chromatography-refractive index detector. The optimization of process variables namely, temperature, flow rate and water to DMF ratio (v/v) for the maximum conversion of DMF have been studied by response surface methodology (RSM) coupled with a Box-Behnken design. The analysis of variance (ANOVA) data shows the conversion of DMF significantly enhances with temperature. Higher flow rate has adverse effect on DMF conversion, whereas water to DMF ratio (v/v) shows negligible effect on conversion of DMF. With the help of a developed RSM model, the highest conversion of DMF (89.82 wt%) was predicted at 1100 °C, 0.48 ml/min and water:DMF ratio of 1.35 (v/v). Based on the experimental design, eight empirical models were developed those depict the interacting effect of different sets of operating variables on conversion of DMF and yield of seven products. Effect of process variables on yield of CO<sub>2</sub> and N<sub>2</sub> were studied, individually. Oxidative pyrolysis of DMF was also investigated, which shows significant reduction in the coke formation with increasing H<sub>2</sub>O<sub>2</sub> to DMF mol ratio.

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## 1. Introduction

In nuclear recycling plants, the irradiated spent fuel is reprocessed to recover U and Pu using PUREX (Plutonium and Uranium extraction) process. Further, during post-PUREX steps, the radioactive waste generated is mainly consisting of minor actinides (Am, Cm and Np) and lanthanides, which has life time of few hundreds to some millions of years. For the systematic and safe disposal of the nuclear waste, the partitioning methods have been studied worldwide, in which minor actinides are first separated from lanthanides by using selective organic extractants and then transmuted to stable nuclides by nuclear reactions, followed by their consequent burning in high flux reactors or accelerators [1,2]. To this end, several solvent extraction methods have been studied with their respective extractants (Table 1) [3–14]. Many of these extraction methods utilize organophosphorus extractants that leave undesirable residual solid waste [15].

Tri-n-butyl phosphate (TBP) is a popular extractant in PUREX process, used for recovery of unused fuel as well as the bred actinides. TBP has the advantages of being more stable, less flammable, excellent solubility in hydrocarbon diluent, having

easier back extraction ability and better separation than other solvents [16]. However, it has several demerits, which prompted perusal of alternate extractants for PUREX process [17,18]. TBP has some solubility in aqueous nitric acid solution (300–400 ppm) [19,20]. A dissolved TBP reacts with nitric acid to form organic nitrates or red oil. Thermal decomposition of red oil in closed evaporators resulted in runaway explosions, which is often mentioned as a big risk factor [21–24]. In the presence of nitric acid and radiations, TBP degrades in mono-butyl phosphate (MBP), di-butyl phosphate (DBP) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) resulting in formation of emulsion or third phase that reduces the extraction efficiency of PUREX process, significantly [25,26]. Further, TBP cannot be incinerated or burned completely, resulting in deposition of high volume of secondary waste phosphates [27]. Recently, the amide-based extractants have being actively explored as efficient alternatives to TBP by many separation scientists and technologists. The N,N,N',N'-dimethyl dibutyl tetradecyl malonamide (DMDBT-DMA), 2,2'-(methylimino) bis (N,N-dioctyl acetamide) (MIDOA) and N,N,N',N'-tetraoctyl diglycolamide (TODGA) are the promising extractants and could separate the minor actinides and lanthanides from radioactive waste [28–32]. After few cycles of solvent extraction process, large amount of used and deformed amide based extractants are discarded those are referred as secondary low level waste. These waste amides are radioactive and could be hazardous to the environment.

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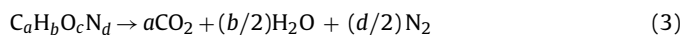
**Table 1**  
Extraction processes to separate U, Pu and minor actinides from spent nuclear fuel.

Solvent extraction process	Extractant
PUREX	Tri-n-butyl phosphate (TBP) in n-alkane diluent [3]
UREX	Tributyl phosphate (TBP) diluted with n-dodecane and acetoacetic acid [4]
American TRUEX	Octyl-(phenyl)-N,N'-diisobutylcarbamoylmethylphosphine oxide (CMPO) with TBP as a phase modifier [5]
Chinese TRPO	Trialkylphosphine oxide [6,7]
Japanese DIDPA	Di-isodecylphosphoric acid with TBP [8–10]
French DIAMEX	N,N'-dimethyl-N,N'-dibutyltetradecylmalonamide (DMDBTDMA) [11–13]
Trivalent actinide lanthanide separations by phosphorus-reagent extraction from aqueous complexes (TALSPEAK)	Di-(2-ethylhexyl) phosphoric acid (HDEHP) [14]

In addition, the elimination of various toxic amides from other chemical industries like fine chemicals, herbicides, organic feed stocks, emulsifiers and pharmaceuticals is also a very critical environmental issue [33,34]. Many amides (e.g., acryl amide) have been reported as potent carcinogenic, mutagenic, teratogenic, neurotoxicants, highly poisonous and environmental pollutants [35–37]. The safe disposal of both radioactive and industrial waste amidic solvents is necessary to minimize their heavy burden to the environment. The amides are completely incinerable as they are composed of C, H, O and N elements. In this study, we report a steam pyrolysis method for the continuous disposal of waste amidic solvents. Superheated steam was selected as a diluent, pyrolyzing media and coke inhibitor. In stainless steel flow reactors, steam converts the high boiling components and coke into CO, CO<sub>2</sub> and H<sub>2</sub> as shown in Eqs. (1) and (2). Steam enables the continuous operation of pyrolytic processes for the disposal of organic wastes, without the necessity of burning carbonaceous deposits separately [38–41].



It is expected that during the incineration of waste amidic solvents, massive amount of gaseous mixtures will be generated at industrial scale and then released in atmosphere. In case of pyrolysis of amidic solvents, following decomposition reaction is expected theoretically;



The products in Eq. (3) are eco-friendly species, but the complete decomposition of amides in only CO<sub>2</sub>, N<sub>2</sub> and water seems to be quite hypothetical. The other possible products such as ammonia, NO<sub>x</sub>, cyanides, amines and lower hydrocarbons can be toxic and would have hazardous effect on the environment. Reports on steam pyrolysis of amides (at more than 500 °C) as a waste management method are not reported in the open literature. Therefore, it becomes important to obtain the experimental data along with detail qualitative and quantitative analysis of all the pyrolysis products at different combinations of reaction conditions. Commonly, in the steam pyrolysis studies, temperature, residence time and water to feed ratio mainly decide the types of the products and their overall composition. In our previous study, we have used a conventional “one-factor-at-a-time” approach to understand the effect of reaction parameters on conversion of dimethyl formamide (DMF) and overall products distribution. Also, we have reported the overall kinetics and possible reaction mechanism for the steam pyrolysis of

DMF [42]. However, the interacting effects of reaction parameters on the conversion of DMF and products composition were not studied. It was laborious and tedious to study the interactive effect of all the process variables collectively, by using a single dimensional approach, in which one factor is varied manually, while others are kept constant [43,44]. In this work, the best response expected is the maximum conversion of DMF and high yield of CO<sub>2</sub> and N<sub>2</sub>.

Considering the pyrolysis reactions taking place simultaneously, to achieve the optimized reaction conditions for the desired response, an effective approach is the statistical treatment of experimental data i.e., response surface modeling (RSM), which involves three major steps: (1) performing experiments by the approach of RSM, (2) estimating the coefficients in a mathematical model, and (3) predicting the response and checking adequacy of the model [45,46]. RSM is being increasingly used to optimize the process variables of complex chemical reactions, such as thermal catalytic cracking of naphtha to obtain useful olefins in high yield [47,48]. In this work, steam pyrolysis of DMF was performed in a SS 316 plug flow reactor as a waste solvent minimization method. DMF was selected as a model compound for the pyrolysis studies. The main aim of this work is to develop the mathematical empirical models that can describe the interactive effect of three key parameters viz. temperature, flow rate and water to DMF ratio (v/v) on conversion and distribution of products. These models are used to carry out the single and multi-objective optimizations and finally, the optimum process conditions are proposed. We believe the process conditions can be optimized in similar manner for multitude of amidic solvents and extractants.

## 2. Experimental

### 2.1. Steam pyrolysis set-up

A laboratory scale steam pyrolysis setup was designed and constructed, as shown schematically in Fig. 1. The preheater–vaporizer assembly (70 cm) incorporated with a pyrolysis plug flow reactor (PPFR) (35 cm) was fabricated by using stainless steel 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 placed in a single zone ceramic furnace (1.2 kW) that was operated up to 1100 °C. The temperature of preheater–vaporizer assembly and that of a PPFR were separately controlled by two temperature regulators. The K-type thermocouples were used to measure the temperature of a reactor wall. The entire reactor setup was compactly insulated by using ceramic wool and encapsulated in aluminum foil to minimize the heat transfer to the surroundings. There was a provision at bottom of the vaporizer to evacuate entire pyrolysis setup by using a vacuum pump. All connections were made by SS 316 ferrule fittings. The non-return valves were also made up of SS 316, whereas poly epoxy-epoxy ketone (PEEK) material was specially used in needle valves so that the valves can withstand high temperature of pyrolytic operations. A PPFR was further equipped with a metal condenser (SS 316, 90 cm) and a metal phase separator with ice-water cooled jacket.

### 2.2. A typical run

To maintain the pyrolytic conditions in PPFR, initially, with the help of a vacuum pump the entire setup was completely evacuated. A dual channel peristaltic pump with individual controls was used to feed distilled water and DMF simultaneously from their containers to the vaporizer and pre-heater, respectively. The non-return valves were used at feed inlets to restrict the back flow of hot reaction mass. The pre-heater–vaporizer and pyrolysis

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