REGENERATION OF SLFO-NITRO ACID MIXTURE IN CONTINUOUS MODE OPERATION

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ABSTRACT

Sulfo-nitro acid mixtures necessary for the production of two types of nitrocellulose (i.e., NC_1 and NC_2) were prepared in a continuous mode, using a lab scale continuous stirred tank reactor. Three variables, which were considered as the most dominant variables in characterizing the performance of the regeneration process, were studied. Speed of stirrer in the range of 80-400 rpm, temperature in the range of 20-40 °C, and residence times in the range of 30-90 minutes were considered. The experimental work was designed via Box-Wilson experimental design, and third order polynomial was proposed to relate the three variables with the concentration of nitronium ion $NO_2^\oplus$. For the first time, nitronium ion concentration was considered to be the contributor of the viability of sulfo-nitro acid mixture for nitrating the cellulose. Two measuring techniques were adopted (i. e., the electric conductivity, and the visible ultra-violate spectrophotometer). The necessity for the process to turn over the batch mode preparation process of the acid mixture that already exists in Al-Qaqa Company was studied carefully. Different samples from high quality nitrocellulose were prepared and tested in account of nitrogen content and chemical stability using the produced mixed acids in continuous mode operation has proved the viability of the measuring technique that was employed in this study besides it was ascertained that good uniformity of the used mixed acid has reached in contrary to the batch process that conveys difficulties in homogeneity. Employing the ideas that were already justified through this study, there is a large opportunity for producing acid mixtures using continuous mode operation was confirmed.
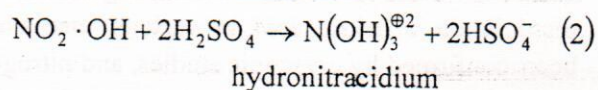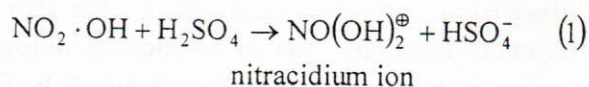
INTRODUCTION

The first attempts to nitrate cellulose by means of mixtures made up from nitric and sulfuric acids were found that increasing the concentration of sulfuric acid in the mixture diminished the rate of the nitration reaction. The pioneer investigators had examined the effect of the composition of mixed acid, and the influence of the nitration temperature within the range from 0 to 80 °C on the nitrogen content of nitrocellulose, the content of non-nitrated cellulose, the yield, the solubility of the products in ether-alcohol mixture and the viscosity of the acetone solution using cotton linters as substrate. From these experiments it has been established that nitrocellulose containing more than 13.5 % N is unstable and readily decomposes.

It was stated by others that two forms of acids exists: True acids with a spectrum similar to that of metal salts and pseudo-acids with a spectrum similar to that of esters. According to Hantzsch (1930), the structure of true nitric acid is, $NO_3^- H^\oplus$ or $N(O_3)^- H^\oplus$. The hydrogen atom is attached by electrostatic force only and that is why it dissociates readily, while the structure of concentrated nitric acid is that of the undissociated pseudo-acid NO_2OH or $N(O_2)OH$. Both forms are in equilibrium. The pseudo-acid form acts as a nitrating and esterifying agent. The addition of water shifts the equilibrium towards the formation of the dissociated form of the true acid, which has no nitrating properties (Urbanski, 1964):

$$NO_2 \cdot OH \xleftarrow{\quad H_2O \quad} NO_3^- H^\oplus$$
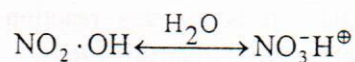
Thus, the addition of sulfuric acid to nitric acid increases the concentration of the pseudo-acid. The sulfuric acid, being the stronger, gives off a proton to pseudo-nitric acid and causes the formation of the following mono-and bivalent ions:

$$NO_2 \cdot OH + H_2SO_4 \rightarrow NO(OH)_2^\oplus + HSO_4^- \quad (1)$$
$$\text{nitracidium ion}$$

$$NO_2 \cdot OH + 2H_2SO_4 \rightarrow N(OH)_3^{\oplus 2} + 2HSO_4^- \quad (2)$$
$$\text{hydronitracidium}$$

In particular, according to Eq (2) in which the $H_3NO_3^{\oplus 2}$ ion is formed, appeared to be correct in the light of Hantzsch's cryometric studies (1930). Thomas *et al* (1940) and Simons *et al* (1941) were stated that it is not only sulfuric acid added to nitric acid that increases the latter nitrating properties, such substances as boron fluoride or hydrogen fluoride when added to nitric acid have a similar effect.
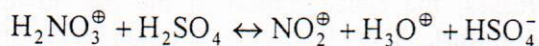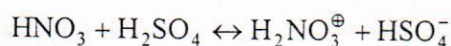
Many authors (Urbanski, 1964, 1984; Finar, 1959; Gillespie and Goraham, 1950) have investigated the reaction between nitric acid and sulfuric acid in batch process. They stated that feed composition, which will be introduced to the process to fortify, will change with time. Such changes may be abrupt, as in switching to feed from another storage tank that contains material of a different composition or they may be contains cyclical-changes.

As many authors on the fact have stated out that nitronium ion $NO_2^{\oplus}$ is the active nitrating agent. According to Finar (1959), the active nitrating agents is the nitronium ion $NO_2^{\oplus}$, which is formed as follows:

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^{\oplus} + H_3O^{\oplus} + 2H_2SO_4^{-}$$

Also Kennedy (1987) found that nitronium ion is the species responsible for nitration, and that the various acid mixtures that gave same conversion contained practically the same concentration of the nitronium ion.

Generally, the presence of acids stronger than HNO_3 accelerates the heterolysis of nitric acid into $NO_2^{\oplus}$ and OH^{-}. It is for this reaction that mixed acid is so effective (Urbanski, 1964).

$$HNO_3 + H_2SO_4 \leftrightarrow H_2NO_3^{\oplus} + HSO_4^{-}$$

$$H_2NO_3^{\oplus} + H_2SO_4 \leftrightarrow NO_2^{\oplus} + H_3O^{\oplus} + HSO_4^{-}$$

The presence of the ion $NO_2^{\oplus}$ also had been confirmed by (Albert and Geoffrey, 1980) that this ion is directly involved, not only in the dissociation of nitric acid itself, but also in nitration reactions and in solution of nitrogen oxides in nitric acid and other strong acids. The dissociation of nitric acid in various media has been confirmed by cryscopic studies, and nitrogen oxides have also been found to confirm the presence of the various ions in such solutions. For example, the $NO_2^{\oplus}$ ion can be identified by Raman line at about 1400 cm^{-1}. The results which had been obtained by Gillespe and Graham, (1950) as a cryometric examinations of solutions of nitric acid in oleum, that results are in agreement with the following equation, postulating formation of the nitronium ion;

$$HNO_3 + 2H_2S_2O_7 \rightarrow NO_2^{\oplus} + HS_2O_7^{-} + 2H_2SO_4$$
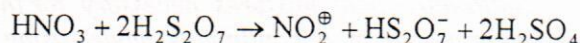
EXPERIMENTAL WORK

Nitric acid of the following composition as listed in Table (1) and of specific gravity 1.503 at 25 °C, freezing point −41.6 °C and boiling point 86 °C was used in the preparation of the nitrating mixture.

Table (1) Analysis of nitric acid

Composition	Weight %
HNO$_3$	98.5
Specific gravity	1.511
Ash content	0.009
Lead salts	0.0097
Sulfate as H$_2$SO$_4$	0.015
Chloride as HCl	0.008
Nitrogen oxides as N$_2$O$_4$	0.45
Fe	0.0087

Fuming Sulfuric Acid (Oleum), the constitution of concentrated oleum is controversial, but with equimolar ratios the major constituent is pyrosulfuric (disulfuric) acid ($H_2S_2O_7$), and it has higher acidity than H_2SO_4 (Albert and Wilkinson, 1980). The analysis of the oleum that was employed in the preparation of the nitrating mixture was listed in Table (2) below.

Table (2) Analysis of nitric acid

Composition	Weight %
H$_2$SO$_4$	106
Pb	0.009
As	0.0088
Chloride as HCl	0.0089
Nitrogen oxides as N$_2$O$_4$	0.45
Ash	0.31

Measuring Techniques

The usual technique that is already followed by the factory in Al-Qaqa Company to check the viability of the acid mixture for nitration was usually lasted 3 hours, the time that takes by the lab factory to check the composition of the mixture. This currency of events violates our postulation in developing and implementing a continuous process in the preparation of the acid mixture for nitration. Therefore, it is possible to assign to the experimental procedure of this study some other instantaneous techniques to check properly the viability of the acid mixture with high reliability. For that reason, monitoring the concentration of nitronium ion, which was regarded as a criterion for the completion of nitric acid and sulfuric acid reaction, by implementing two techniques (the electrical conductivity technique and UV spectrophotometer technique) was suggested in order to coincide with the needs of our experimental work.

Electrical conductivity technique

In this work, since electrical conductivity was selected as a convenient continuous measure of the reaction content, the regeneration of mixed acid was followed by monitoring the concentration of nitronium ion $NO_2^\oplus$ in the solution in view of the ionic nature of the products of below reaction.

$$2H_2SO_4 + HNO_3 \Leftrightarrow 2HSO_4^- + H_3O^\oplus + NO_2^\oplus \quad (3)$$

The electrical conductivity of the solution was measured via platinum electrodes. Two devices (WTW LF 521 digital, and AMEL Model 123) were used to ascertain the results where both instruments measures almost similarly although mean values were considered. Cell constants (L) was determined by standards of known concentrations of KCl. Calibrated curve for mixed acid solutions at different temperatures, which have known nitronium ion concentrations against specific conductance were established. These readings are summarized in Table (3) and figured in Fig (1)

Ultraviolet spectrophotometer technique

Concentration of $NO_2^\oplus$ ions in admixture was monitored by Ultraviolet Visible Recorder Spectrophotometer (Type, Shimadza U.V 160 A) in absorption spectrum λ_{max} 265 nm.

Table (3) measured conductivities (mS cm^{-1}) for known $NO_2^\oplus$ concentration in mixed acids at different temperatures

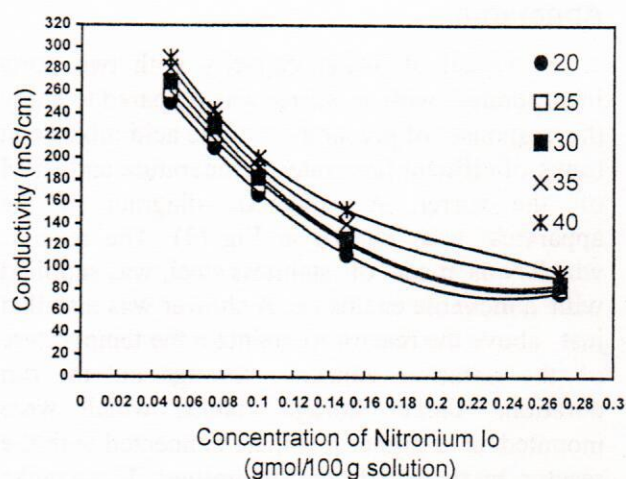| Mixed acids of known $NO_2^\oplus$ Conc. (Urbanski, 1964)				Conductivity (mS cm^{-1})				
HNO$_3$ wt %	H$_2$O wt %	H$_2$SO$_4$ wt %	$NO_2^\oplus$ gmol/100g	20°C	25°C	30°C	35°C	40°C
10	36	54	0.050	250	260	264	281	290
12	30	58	0.075	210	230	228	235	243
13	25	62	0.100	167	175	182	191	200
20	14	66	0.150	112	125	126	140	153
25	10	65	0.270	77	80	84	90	95

Fig. (1) Calibration curves for nitronium ion concentration in mixed acid solution at different temperatures

For quantitative analysis, different concentrations of mixed acids had been prepared and the absorption spectra at λ_{max} 265 nm was measured for these admixtures. The results was listed in Table (4) and shown in Fig (2).

Table (4) Absorption spectra at λ_{max} 265 nm for different mixed acids compositions

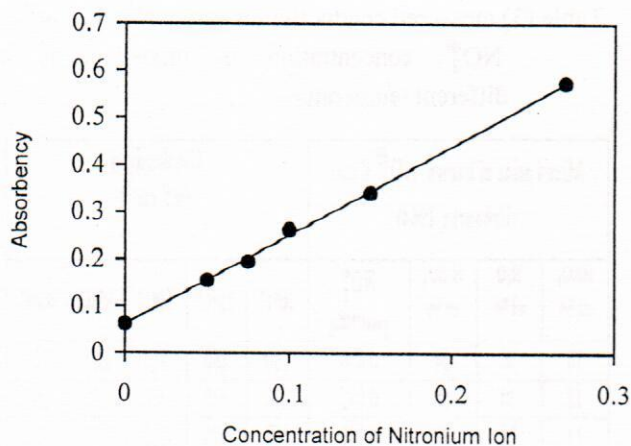| Mixed acids of known $NO_2^\oplus$ Conc. (Urbanski, 1964)				Measured ABS. By UV Spectrophotometer
HNO$_3$ wt %	H$_2$O wt %	H$_2$SO$_4$ wt %	$NO_2^\oplus$ mol/100gm	
-	100	-	0.000	0.062
10	36	54	0.050	0.155
12	30	58	0.075	0.195
13	25	62	0.100	0.263
20	14	66	0.150	0.341
25	10	65	0.270	0.574

Fig (2) Absorption spectra at wavelength λ_{max} 265 nm for different mixed acids

Apparatus

A vessel of 3-liter capacity with two ports incorporated with a stirrer was prepared to study the response of preparation of the acid mixture in terms of effluent flow rates, temperature and RPM of the stirrer. A schematic diagram of the apparatus was shown in Fig (3). The reactor, which was made of stainless steel, was supplied with a movable enclosure. A shower was installed just above the reactor to maintain the temperature of the solution constant through out the run duration. Three storage tanks, which were mounted at a higher level, are connected with the reactor by three different streamlines. These tanks are contained concentrated nitric acid (98 %), sulfuric acid (106 %) as oleum and spent acid (i.e., the recycle stream from nitration process). The spent acid was made similar to the composition of the acid mixture that was feeding back from nitration process of nitrocellulose.
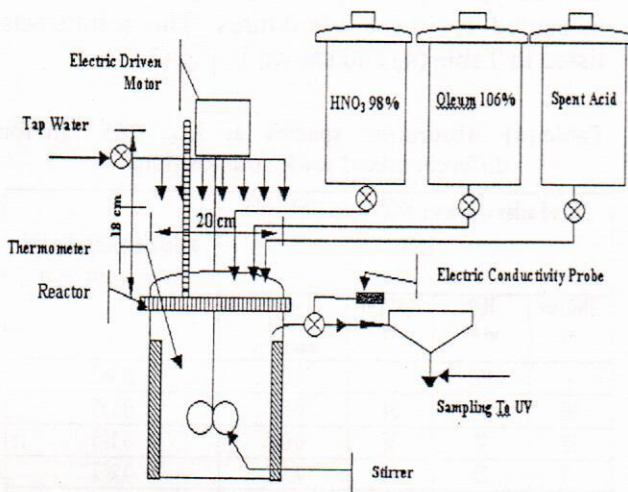
Experimental Procedure

Two sets of experiments were carried out, the first was for preparation of mixed acid to process nitrocellulose with high nitrogen content, NC_1 (e.g. N % = 13.2-13.4). The second was for mixed acid preparation of processing nitrocellulose with low nitrogen content, NC_2 (e.g., N % = 11.3-12.6).

Basically, all the experiments were planned according to Box-Wilson experimental design method. Before each experiment, mass balance has been performed to justify the flow rates of the three streams (spent acid, the nitric acid and the oleum), which were drawn from their tanks. Before permitting the acids from the storage tanks to flow, the reactor was filled with the three types of acid in same proportion as specified and agitation of the mixture was conducted for some time (5 minutes).

The reaction between the mixture commenced vigorously and nitrogen gases were driven out through the exhaust. Water from a shower was directed over the reactor to maintain the temperature of the reactor at a pre-designed value. Electric conductivity and absorbency via UV spectrophotometer of the outcoming stream was recorded throughout the experiment. The experiment was terminated where no variations in electric conductivity were noticed. The sequence of experiments according to central composite design was found in Table (5) below.

Table (5) Sequence of experiments according to central composite design

Exp. No.	Coded Variable			Real Variable		
	X_1	X_2	X_3	Temperature, °C	Time, min	Stirrer Speed, rpm
1	-1	-1	-1	24	42.5	147
2	-1	-1	1	24	42.5	332
3	-1	1	-1	24	77.5	147
4	1	-1	-1	35	42.5	147
5	-1	1	1	24	77.5	332
6	1	-1	1	35	42.5	332
7	1	1	-1	35	77.5	147
8	1	1	1	35	77.5	332
9	-1.732	0	0	20	60	240
10	1.732	0	0	40	60	240
11	0	-1.732	0	30	30	240
12	0	1.732	0	30	90	240
13	0	0	-1.732	30	60	80
14	0	0	1.732	30	60	400
15	0	0	0	30	60	240
16	0	0	0	30	60	240
17	0	0	0	30	60	240
18	0	0	0	30	60	240
19	0	0	0	30	60	240
20	0	0	0	30	60	240

Fig. (3) Layout of the apparatus

RESULTS AND DISCUSION

Statistical Analysis

Experimental designs are frequently performed in the study of empirical relationships between one or more measured responses and a number of variables. The relationship between the concentration of nitronium ion $NO_2^\oplus$ as a response for continuous stirred tank reactor and three variables (i.e., speed of stirrer, temperature and residence time) correlated by a third order polynomial function is determined by carrying out a set of experiments according to central composite design. A nonlinear analysis was carried out to estimate the coefficients of the correlation and optimum conditions were obtained.

To study the significance of each term in the correlated model a statistical analysis was performed. This significance was estimated by comparing the values of b_v^2/Sb_v^2 to the critical value of the F distribution at 90 % level of confidence with 1 and 6 degrees of freedom. The estimated variance of coefficients Sb_v^2 are calculated by the following formula:

$$Sb_v^2 = \frac{S_r^2}{\sum V_i^2} \qquad (4)$$

where V_i is the general symbol for coded variable X_k or interaction variable $X_k X_k$ or centered variable. Whereas, S_r^2 is the estimate of the experimental error variance which is obtained by dividing the residual sum of squares $\sum e_i^2$ by γ (i.e. number of degree of freedom). The values of residual error (e_i) are calculated from the difference between the response of the ith experiment (y_i) and the estimated response for the ith experiment $(\acute{y}_i)$.

The results of confidence are tabulated in Table (7) and (8). These results had postulated that for mixed acids of NC_1 type, only term of X_1, X_2, X_1^2 and X_1^3 are significant. Whereas, for NC_2 mixed acid, only X_1, X_2, X_3, X_1^2, X_2^2 and X_1^3 are significant. Accordingly best fitting response functions is then conveniently written for both types as:

For NC₁:

$$Y_{NO_2^\oplus} = 0.214411 + 0.018766X_1 + 0.007119X_2$$
$$- 0.00684X_1^2 - 0.00694X_1^3 \qquad (5)$$

For NC₂:

$$Y_{NO_2^\oplus} = 0.13728 + 0.009529X_1 + 0.005468X_2 +$$
$$0.002472X_3 - 0.00303X_1^2 - 0.00219X_2^2 \qquad (6)$$
$$- 0.00348X_1^3$$

Optimum values of the studied variables at the highest nitronium ion concentration were determined through implementing Hooks and Jeeves optimization method. The optimum conditions in coded and real values are listed in Table (6) for the two sets of experiments.

Table (6) Optimum conditions in coded and real forms for both sets of experiments

	In Coded Forms			In Real Forms		
	X_1	X_2	X_3	rpm	Temp., °C	Time, min
NC₁	0.75	1.391	1.289	309	38	82
NC₂	0.73	0.969	1.048	306	36	78

Effect of Studied Variables on Response Function

To emphasize the effect of each variable on nitronium ion concentration clearly and individually, the response function was predicted by varying one variable, and keeping the other variables constant at predetermined optimum conditions.

In general, comparison between the figures of the two types of acid mixtures illustrates that nitronium ion concentration had considerably fallen as the content of water was increased (i.e., the values of ion concentration for NC_2 acid mixture is less than that of NC_1 acid mixture). At the same time, with increasing the concentration of nitric acid the dissociation reaction would facilitate the generation of nitronium ion. This was found in good agreement with the postulation of Chedin (1949) in addition to the related conclusions which were pointed out by Bruely (1930) who illustrates that the increase in nitronium concentration in case of NC_1 is due to the formation of less mobile ion (i.e., $H_2NO_3^\oplus$). This ion is the principal agent for nitrating according to Hantzsch theory.

Figure (4) to (6) show the effect of one variable at constant other two variables on nitronium ion for NC_1 mixed acid. Whereas, Fig

(7) to (9) show the effect of studied variables for NC$_2$ acid mixture. The statistical analysis of the response functions, Eq (5) and (6) has shown nitronium ion concentration dependence on speed of stirrer (X$_1$), temperature of reaction (X$_2$), and residence time (X$_3$) in following sequence X$_1$ > X$_2$ > X$_3$ for NC$_1$ acid mixture, and also same category was found for NC$_2$ acid mixture.

Fig (4) shows the pronounced effect of speed of stirrer on nitronium ion concentration of NC$_1$ acid mixture. Curvature dependence on stirrer speed was observed that was ascertained from significant analysis. The justification was shown in Eq (5) and Table (7) that nonlinear dependence of nitronium ion concentration on stirrer speed represented was found. Figure (4) shows an increasing attitude of nitronium concentration to some maximum limit (rising function) and then followed no variation of nitronium concentration with higher stirrer speed. The first rising period of nitronium ion concentration dependence occurred in the course of encouraging the reaction between oleum 106 % and nitric acid 98 %, since mixing effect or intensity of mixing increases with increasing stirrer speed. Whilst, no increasing attitude was attributed to lower mixing intensity with increasing stirrer speed (i.e., stagnant region was occurred). Also, decreasing in ion concentration with speed of stirrer higher than 80 rpm may be attributed to the formation of adduct compound (HNO$_3$)$_3$.H$_2$SO$_4$. The last explanation came in agreement with Hackel (1961) who pointed out that the complex compound has been removed slowly as agitation of acid mixture increases.

Temperature effect on nitronium ion concentration was accounted for in Eq (5) with higher positive dependence in comparison to the effect of residence time. The variation of nitronium ion concentration with temperature as shown in Fig (5) shows linear dependence. This dependence was also ascertained through significant analysis study where only X$_2$ had significant effect, Table (7). Herein, the behavior for an isothermal curve had shown different manner where rising response was observed and maximum value was found that attributed in the first rising response to pronounce effect of increasing mixing intensity due to increasing stirrer speed. While the decreasing of nitronium concentration as previously outlined was mainly

attributed to the generation of stagnant pockets. In Fig (7) when residence time was altered keeping constant stirrer speed and temperature, the curve has little variation as already figured out from examining Eq (6), which means no dependence on residence time was recognized. However, decreasing responses near the rear region of the curve was found in Fig (6) which might only contributed to increasing negativity of temperature dependence as side reactions between sulfuric acid and nitric acid were enhanced and lead to the formation of nitrosylsulfuric acid HNOSO$_4$.

The minor dependence of residence time was attributed to the reaction between sulfuric acid and nitric acid that actually occurs instantaneously. This was clearly found from comparing the time dependence of nitronium concentration of both acid mixtures that obviously shows higher dependence of residence time on nitronium concentration for the NC$_1$ acid mixture from that for NC$_2$ acid mixture as the reaction for NC$_1$ proceed faster than that for NC$_2$.

In Fig (7), maximum response was found. Obviously, the behavior was attributed in the first rising response to increase in mixing intensity, but herein, maximum point was found which means a decreasing response occurred that was directly attributed to pronounced negative dependence of temperature and positive dependence speed of stirrer devote.

In studying the effect of temperature on nitronium ion concentration, Fig (8), it was shown that nitronium ion exhibits an extraneous behavior at stirrer speed and residence time equal to 1.732, 1 and −1.732. However, this behavior has not been recognized from statistical analysis calculations. It shows entirely opposite images especially at stirrer speed and residence time coded values of −1.732 and 1.732. Accordingly, one can justify that temperature has an enormous effect on nitronium ion concentration so in-site measuring of nitronium ion concentration instantaneously was advocated via an instrumental technique to monitor and to overcome the difficulties that encountered in nitration step. Same attitude was observed from Fig (9) at stirrer speed and residence time coded value −1.732 where second order dependence at −1.732 was postulate and linear dependence at other values were observed.

Table (7) Analysis of variance of variable effects for NC_1 mixed acid

	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	X_1^2	X_2^2	X_3^2	X_1^3	X_2^3	X_3^3	$X_1X_2X_3$
B	0.018766	$7.119*10^{-1}$	$5.323*10^{-1}$	$1.986*10^{-1}$	$1.8*10^{-6}$	$4.476*10^{-1}$	$-6.84*10^{-1}$	$-4.52*10^{-1}$	$-3.5*10^{-1}$	$-6.94*10^{-1}$	$-3.51*10^{-2}$	$-5.43*10^{-2}$	$2.45*10^{-2}$
Sb^2	$1.2*10^{-3}$	$1.2*10^{-3}$	$1.2*10^{-3}$	$2.0*10^{-3}$	$2.0*10^{-3}$	$2.0*10^{-3}$	$9.26*10^{-4}$	$9.26*10^{-4}$	$9.26*10^{-4}$	$3.1*10^{-1}$	$3.1*10^{-1}$	$3.1*10^{-1}$	$2.0*10^{-3}$
F-value B^2/Sb^2	29.3	4.3	2.36	0.2	$1.6*10^{-5}$	1.0	5.05	2.2	1.3	15.53	0.03	0.09	0.003
F(1,6)=3.78 0.9 Confidence	S	S	NS	NS	NS	NS	S	NS	NS	S	NS	NS	NS

Table (8) Analysis of variance of variable effects for NC_2 mixed acid

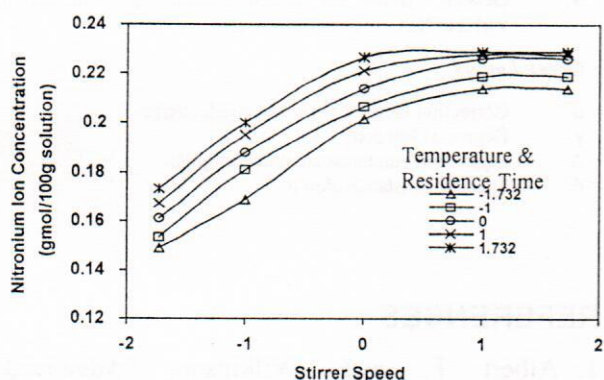|	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	X_1^2	X_2^2	X_3^2	X_1^3	X_2^3	X_3^3	$X_1X_2X_3$
B	0.009529	$5.468*10^{-1}$	$2.472*10^{-1}$	$-4.89*10^{-2}$	$-2.64*10^{-2}$	$4.82*10^{-2}$	$-3.03*10^{-1}$	$-2.19*10^{-1}$	$-8.6*10^{-2}$	$-3.48*10^{-1}$	$-6.92*10^{-2}$	$-4.49*10^{-2}$	$7.62*10^{-2}$
Sb^2	$1.37*10^{-6}$	$1.37*10^{-6}$	$1.37*10^{-6}$	$2.4*10^{-6}$	$2.4*10^{-6}$	$2.4*10^{-6}$	$1.07*10^{-6}$	$1.07*10^{-6}$	$1.07*10^{-6}$	$3.51*10^{-7}$	$3.51*10^{-7}$	$3.51*10^{-7}$	$2.4*10^{-6}$
F-value B^2/Sb^2	66.3	21.8	4.46	0.09	0.03	0.1	8.6	4.5	0.7	34.5	1.36	0.57	0.24
F(1,6)=3.78 0.9 Confidence	S	S	S	NS	NS	NS	S	S	NS	S	NS	NS	NS

Fig (4) Effect of stirrer speed on nitronium ion concentration at constant temperature and residence time for NC_1 acid mixture
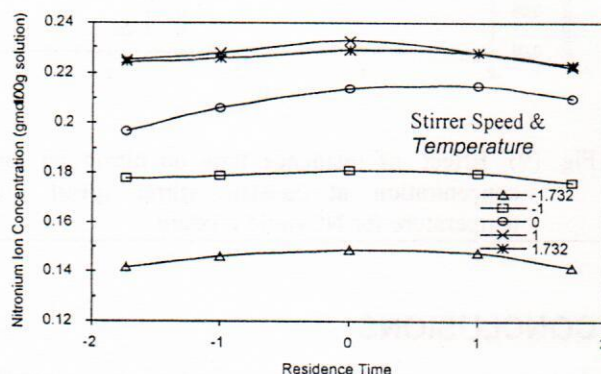

Fig (6) Effect of residence time on nitronium ion concentration at constant stirrer speed and temperature for NC_1 acid mixture
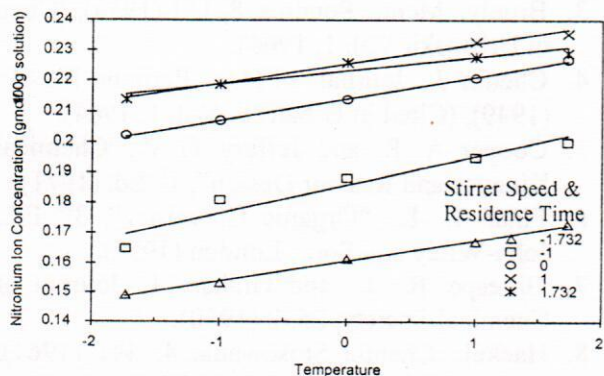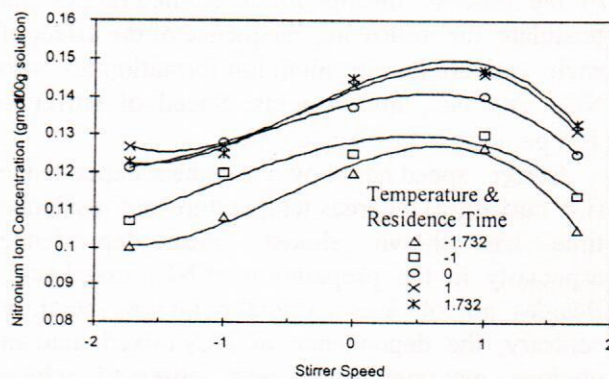

Fig (5) Effect of temperature on nitronium ion concentration at constant stirrer speed and residence time for NC_1 acid mixture

Fig (7) Effect of stirrer speed on nitronium ion concentration at constant temperature and residence time for NC_2 acid mixture
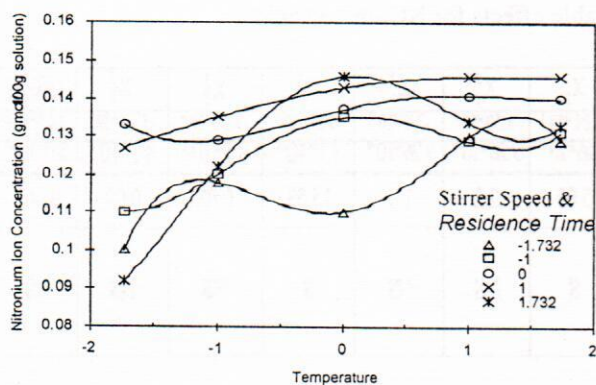
Fig (8) Effect of temperature on nitronium ion concentration at constant stirrer speed and residence time for NC$_2$ acid mixture
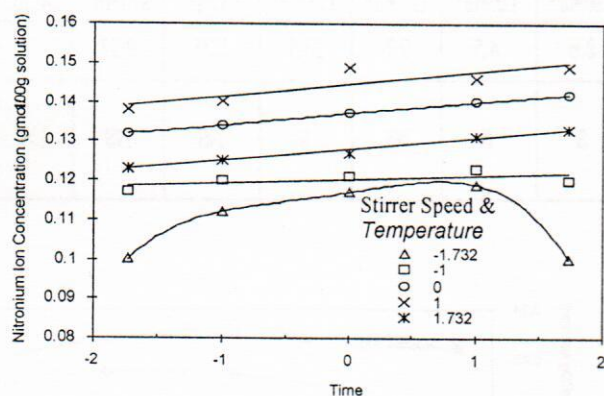

Fig (9) Effect of residence time on nitronium ion concentration at constant stirrer speed and temperature for NC$_2$ acid mixture

CONCLUSIONS

Two mathematical models for $NO_2^{\oplus}$ concentration in terms of stirrer speed, temperature and residence time were developed. Both equations adequately describe the behavior of the process throughout the studied ranges and postulate the following sequence of the effect of each variable on nitronium ion formation for both NC$_1$ and NC$_2$ mixed acids: Speed of stirrer > Temperature > Residence time

Stirrer speed has shown nonlinear dependence (i.e. curvature) whereas temperature and residence time has shown almost linear dependence especially in the preparation of NC$_1$ mixed acid. Besides no obvious maximal point was found. In contrary, the dependence of NC$_2$ mixed acid an obvious maximal point was observed, where stirrer speed and temperature have shown nonlinear dependence. Almost positive dependence of the response function has observed

except reverse attitude was noticed at speed of stirrer over 310 rpm and temperature higher than 40 °C.

The analysis of variance for NC$_1$ mixed acid data shows significant effect of only four terms (i.e., X_1, X_2, X_1^2 and X_1^3) where six terms had shown significant effect in the preparation of NC$_2$ mixed acid (i.e., X_1, X_2, X_3, X_1^2, X_2^2, and X_1^3).

NOMENCLATURE

e_i	Residual error
e_i^2	Residual sum of squares
k	Number of variable
k, k$_c$	Specific conductance mho cm^{-1}
L	Conductance ohm^{-1}
L	Length of conductivity cell (region between the electrodes m
R	Resistance ohm
R	Speed of stirrer rpm
y_i	Response of the ith experiment
y_i'	Estimated response for the ith experiment
T	Operating temperature °C
t	Residence time min
S_r^2	Estimate of the experimental error variable
V_i	General symbol for coded variable X_k or interaction variable X_kX_k or centered variable

Greek Letters

α	Correction factor for specific conductance
γ	Degree of freedom
Λ	Equivalent conductance mho cm^2/gmol
P	Specific resistance ohm m

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