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Kinetics Studies on Esterification Reaction of Acetic acid with Iso-amyl Alcohol over Ion Exchange Resin as Catalysts

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Abstract : In this work, the esterification of acetic acid with iso-amyl alcohol catalyzed by acidic ion-exchange resins (TULSION^R T-62, T-63 and T-66 MP) has been investigated in a batch reactor to determine the intrinsic reaction kinetics. Iso-amyl acetate is synthesized in this reaction, has the fragrance of strong odor (similar to both banana and pear). The effects of various parameters on the rate of reaction (such as temperature, mole ratio, catalyst loading, and stirrer speed) are studied. The solid-liquid external mass transfer resistance as observed using various stirring speeds is absent and the rate of reaction depends on temperature. Further pseudo-homogenous model is developed for an intrinsically kinetically controlled reaction, which is free from either intra-particle diffusion or external mass transfer resistance. The rate expression developed in this work would be useful in the simulation and design of reactive distillation column for the production of iso-amyl acetate. The resultant kinetic model fitted the experimental data well. The activation energy is found to be 41.88 kJ/kmol for the formation of iso-amyl acetate.

Keywords: *acetic acid, iso-amyl alcohol, iso-amyl acetate, esterification, ion-exchange resins, kinetics, reactive distillation.*

1. Introduction

The low molecular weight organic esters have pleasing smell and are found in applications in the food industry for synthetic essence and perfume. Esterification reactions are ubiquitous reactions especially in pharmaceutical, perfumery and polymer industries, wherein; both heterogeneous and homogeneous catalysts have been extensively used. Iso-amyl acetate (or Iso-pentyl acetate) is often called as banana oil, since it has the recognizable odor of this fruit. Iso-amyl acetate is synthesized by esterification of acetic acid with iso-amyl alcohol. (Eq.1). Since the equilibrium does not help the formation of the ester, it must be shifted to the right, in favor of the product, by using a surplus of one of the starting materials. Iso-amyl acetate is a kind of flavor reagent with fruit taste. The use of H_2SO_4 often originates the problems such as corrosion for equipments and pollution for environment.

$$CH_3\text{-}COOH + C_5H_{11}\text{-}OH \xleftrightarrow{k} C_5H_{11}\text{-}COO\text{-}CH_3 + H_2O \qquad (1)$$

The reaction of equation (1) progress very slowly in the absence of acid catalysis. Therefore, both homogeneous and heterogeneous catalysis can be used. Although homogeneous catalysts such as sulfuric acid, p-toluene sulfuric acid, and hydrochloric acid have a strong catalytic effect, they can cause some issues such as the development of side reactions resulting in a corrosive environment by the discharge of acid-containing waste. [2]. It also results in sulfur contamination of the final product, which is unacceptable. Further, the use of homogeneous catalyst requires neutralization with an alkali, which leads to severe effluent problems on industrial scale. In all kinetic studies done with ion-exchange resins as catalysts, acidic ion-exchange gel-type styrene-divinyl benzene (DVB) resins have been used [3].Research in catalysis by ion exchange resins is undeniably interesting, not only from a purely physicochemical point of view but also in terms of the advantages of these types of catalyst over the conventional ones. Ion exchange resins increase the product yield, keep their activity a long time, and do not pollute. Ion exchange resins separate from reaction media easily and they regenerate easily for reuse [4,5,6,7,8] Heterogeneous catalysts such as zeolites, ion-exchange resins, and acidic clay catalysts are gaining importance of high purity of products, because they are easily removed from the reaction mixture and have lower corrosive effects [7] The solid acid catalysts are non-corrosive, easy to separate from the reaction mixture and a variety of reactor types and configurations can be adopted on industrial scale. They can also be used repeatedly over prolonged period of time without any difficulty in handling and storing. [2]

Most reactions catalyzed by ion exchange resins can be classified as either quasi-homogeneous or quasi-heterogeneous. The kinetics of this model reaction catalyzed by Amberlyst-15 was described in previous investigations with both a quasi-homogeneous and a quasi-heterogeneous model. [9] A common method of operating equilibrium-limited reactions is to use an excess of one reactant in order to increase the conversion of the limiting reactant. In reactive distillation (RD), the continual separation of products from reactants forces the reaction to surpass the equilibrium conditions. RD is a process where separation of the components of a reaction system is accompanied by a chemical reaction in a column.

1.1 Kinetic Model

The kinetics of esterification reaction can be expressed using a simple Pseudo-homogenous model or more complicated models based on the Langmuir-Hinshelwood Hougen-Watson (LHHW) mechanism or Eley-Rideal (ER) mechanism in the absence of any intraparticle diffusional limitations. Pseudo-homogenous first and second order models are applicable to many ion-exchange resin catalyzed reactions and highly polar reaction medium. [2]

1.1 Pseudo-homogenous Model

Among all the models, the simplest model is the Pseudo-homogenous model. Consider reaction given by equation (2). The rate expression for this reaction is given by:

$$-r_{CH_3COOH} = k_1\, C_{CH_3COOH}\,.C_{C_5H_{11}OH} - k_2\, C_{C_5H_{11}COO\,CH_3}\,.C_{H_2O} \qquad [2]$$

The reaction equilibrium constant is given by

$$K = \frac{k_1}{k_2} \qquad [3]$$

The reaction equilibrium constant is calculated from

$$\ln\frac{K}{K^0} = \frac{\Delta H_R^{o(l)}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \qquad [4]$$

where, $K^0 = \exp\left[\frac{\Delta G_R^{o(l)}}{RT_0}\right]$ [5]

Esterifications reactions are known to be second order reversible reactions. Therefore, for the bimolecular type second order reactions,

$$A + B \leftrightarrow C + D \qquad [6]$$

With restrictions that,

$C_{AO} = C_{BO}$ and $C_{CO} = C_{DO} = 0$

The rate expression can be written as,

$$-r_B = \frac{-d_{CB}}{dt} = C_{BO}\frac{dX_B}{dt} = k_1 C_A.C_B - k_2 C_C.C_D$$
$$= k_1 C^2{}_{BO}\,(1 - X_B)^2 - k_2\,(C_{BO}X_B)^2 \qquad [7]$$

where,
A= acetic acid
B= iso amyl alcohol
C= iso amyl acetate
D= water

At the equilibrium, $-r_B = 0$

Hence from the above equations, we determine the fractional conversion of B at the equilibrium condition by following equation:

$$K = \frac{C_{Ce},C_{De}}{C_{Ae}.C_{Be}} = \frac{X^2{}_{Be}}{(1 - X_{Be})^2} \qquad [8]$$

The equilibrium constant is given by equation [9] as,

$$\mathrm{K} = \frac{\mathrm{k}_1}{\mathrm{k}_2} \qquad [9]$$

Combining equation [3], [7] and [9] in terms the equilibrium conversion, we obtain,

$$\frac{-d_{XB}}{dt} = k_1 C_{BO}\left[(1 - X_B)^2 - (1 - \frac{X_{Be}}{X_{Be}}).\,X^2{}_B\right] \qquad [10]$$

With conversions measured in terms of $X_{Be,}$ this may be indicated as a pseudo second-order reversible reaction, which on integration gives,

$$\ln\left[\frac{X_{Be} - (2X_{Be} - 1).X_B}{X_{Be} - X_B}\right] = 2k_1\left(\frac{1}{X_{Be}} - 1\right)C_{BO}.t \qquad [11]$$

1.2 Temperature and reaction rate*:*

We can examine the variation of the rate constant with temperature by Arrhenius law relationship,

$$k_1 = k_1^o \exp\left[\frac{E_A}{RT}\right] \qquad [12]$$

This is conveniently determined by plotting $\ln k_1$ versus 1/T.

2. Previous Studies

Iso-amyl acetate synthesis reaction was studied in the presence of various solid acid catalysts in the past. [10] studied the kinetic behavior catalyzed by acidic cation exchange resin, Amberlyst 15. The kinetic data were correlated by a quasi-homogenous (QH) model with which the apparent rate constants at each reaction temperature were determined. They reported the activation energies of the forward and backward reactions as 51.74 kJ/mol and 45.28 kJ/mol respectively. Further they investigated the kinetic behavior of the heterogeneous esterification of acetic acid with amyl alcohol over an acidic cation-exchange resin, Dowex 50Wx8-100. [9, 10]

Teo et al, (2004) presented kinetics of heterogeneous catalyzed esterification of acetic acid with iso amyl alcohol with a cation-exchange resin catalyst, Purolite CT-175, in a stirred batch reactor. Effects of various parameters such as speed of agitation, catalyst particle size, and mole ratio of reactants, reaction temperature, catalyst loading, and reusability of the catalyst were studied to optimize the reaction condition. The kinetic data were correlated with the Langmuir–Hinshelwood–Hougen–Watson model. Saha et al, (2005) studied the reaction kinetics with dilute acetic acid. The kinetic data were correlated with Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (E-R) models. They presented detailed kinetic data and a reliable rate expression for the esterification of acetic acid with iso-amyl alcohol that would be useful for the simulation and design of an RDC for removing dilute acetic acid from aqueous streams.

Steinigeweg et al, (2002) reported the reaction kinetics for butyl acetate system using Amberlyst 15 as a catalyst and the kinetic constants for a pseudo-homogenous kinetic model are presented. Gangadwala et al, (2003) studied the esterification of acetic acid with *n*-butanol in the presence of ion-exchange resin catalysts such as Amberlyst-15 to determine the intrinsic reaction kinetics. In their work, kinetic modeling was performed to obtain the parameters related to intrinsic kinetics.

Pseudo-homogenous, (PH), Eley-Rideal (ER), Langmuir-Hinshelwood-Hougen-Watson (LHHW), and modified LHHW models were presented.

Tang et al, (2005) presented an excellent review on the esterification of acetic acid with five different alcohols, ranging from C_1 to C_5 and presented data for reaction kinetics and phase equilibrium. Schmitt et al, (2006) presented reaction equilibrium and kinetics for *n*-hexyl acetate synthesis in batch reactor using Amberlyst CSP2 as a catalyst. Two kinetic models are tested, a pseudo-homogeneous and an adsorption-based model and shown that despite its simplicity, the pseudo-homogeneous model gives better results and was recommended for further use.

The objectives of the present study were to study kinetic behavior of esterification reaction between iso-amyl alcohol and acetic acid catalyzed by an acidic ion-exchange resin (TULSION^R T-63, MP) in a batch reactor to determine the intrinsic reaction kinetics and test the applicability of the macro porous cation-exchange resin as a catalyst for the esterification reaction. Batch kinetics studies are performed in batch reactor to determine the parameters for different kinetic models, which, can further be used to model the same reaction in RD column.

3. Experimental

3.1 Chemicals:

Acetic acid (99.8%) and iso-amyl alcohol (99%) are purchased from Merck India Ltd., Mumbai. Iso-amyl acetate (> 99% purity) is purchased from s.d. Fine chemicals Ltd., Mumbai and distilled water is used for experimental work. All chemicals are used without further purification.

3.2 Catalysts:

The macroreticular ion exchange resin, TULSION^R T-63, MP, (Courtesy Thermax India, Ltd.) was used in this study. It is a strongly acidic and macroreticular polymeric material based on cross-linked styrene divinyl benzene copolymers. A pretreatment procedure is applied to the catalyst before use. The catalyst was washed with methanol and water to separate the impurities. The washed catalyst is kept in a vacuum oven at 348 K until the water content was completely removed. The physical properties of the catalyst employed for this reaction are listed in the Table 1.

3.3 Apparatus

The experiments are carried out in a stirred batch reactor consisting of a *water* jacket as shown in Figure 1. The experimental set-up consists of heating chamber whose temperature can be set independently. The reaction is performed in a 750 ml glass reactors equipped with stirrer and condenser and placed in heating chambers for the accomplishment of the required temperature. A reflux condenser was fitted to the reactor to prevent a massive loss of the reaction mixture. A motor drives the stirrer with a control over the speed of agitation. The speed can be measured using a non-contact type tachometer. Digital temperature indicator is provided to measure the temperature of the reaction mixture in the reactor.

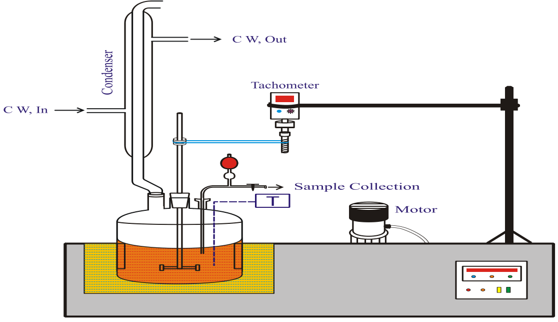

Figure 1 Schematic diagram for batch reaction kinetics studies [10]

3.4 Reaction Procedure and Analysis

Experiments are carried out at various molar ratios of acetic acid and iso-amyl alcohol at temperatures of 363 to 403K at different catalyst loading: 3.0, 5.0, 7.0 and 10.0 gm per 100 gm acetic acid, Mole Ratio: 1:1, 2: 1, 1:2 and 3: 1, Stirrer speed: 400 rpm to 1200 rpm.

Acetic acid and catalyst are charged into the reaction vessel. The volume of the reaction mixture remained almost constant (700 ml) during all experiments. After the desired temperature is reached, iso-amyl alcohol preheated to the same temperature is quickly poured into the reactor. This moment was taken as the beginning of the reaction. Several samples of approximately 500 microlitres were taken for analysis. At the beginning of the experiments, samples are taken every 20 min, but towards the end of the experiments samples are drawn from the reactor every hour, until completion. Repeating three experimental runs under identical conditions checked the reproducibility of the experimental data. The reproducibility is of the order of $\pm 5\%$ of conversion of the limiting reactant.

Gas chromatography is used for the analysis of the different samples from the different locations of RD column. Acetic acid, iso-amyl alcohol, iso-amyl acetate and water are analyzed using gas chromatograph (Model C-911, Mak Analytica India Ltd.) which is equipped with thermal conductivity detector (TCD). The samples are analyzed Porapak Q with hydrogen as carrier gas at a flow rate of 5×10^{-7} m^3/s. The injector and detector are maintained at a temperature of 493K and 423K respectively. The oven temperature is maintained isothermally at 513K to get the best resolution in less time.

The results obtained by GC are confirmed by independent titration using standard sodium hydroxide (NaOH) solution using phenolphthalein as indicator. The reliability of the titration method is confirmed with the help of analysis of standard samples containing iso-amyl acetate to ensure the hydrolysis of ester does not takes place during the course of titration. Acetic acid concentration is cross-checked by titrating the sample with dilute 0.1 N sodium hydroxide solution using phenolphthalein as indicator. The analytical relative uncertainty is <5%, which is good enough within the acceptable limits.

The conversion of iso-amyl alcohol, the limiting reactant, at different intervals of time is shown in Figure 2. It is seen that the speed of agitation had no effect of conversion beyond 1000 rpm and thus there is no restriction of external mass transfer of iso-amyl alcohol, from bulk liquid phase to the outer surface of the catalyst beyond this speed. Further experiments are conducted at 1000 rpm.

4.2 Effect of Catalyst Loading

In the absence of mass transfer resistance; the rate of reaction is directly proportional to catalyst loading based on the whole volume of the liquid phase. The catalyst loading is changed from 3 to 10 gm dry-resin at a temperature of 383 K, feed mole ratio of 2:1, and stirrer speed of 1000 rpm. Figure 3 shows the plot of conversion versus time at different catalyst loadings. It can be observed that the rate of reaction increases as the catalyst loading is increased.

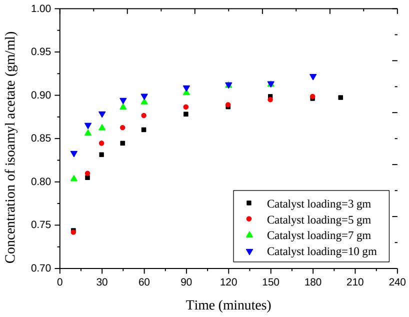

Figure 3 Effect of catalyst loading on iso-amyl acetate concentration

Temperature =383K, Mole ratio= 2:1, Stirrer Speed: 1000 rpm, Catalyst: TULSION MP T-63, Particle size=0.2- 1.3 mm

4. 3 Effect of Mole Ratio

Esterification of acetic acid with iso-amyl alcohol is an equilibrium-limited chemical reaction and because the position of equilibrium controls the quantity of ester formed, the use of an excess of iso-amyl alcohol enhances the conversion of acetic acid. The initial molar ratio of iso-amyl alcohol to acetic acid was varied from 1: 1 to 3:1 at a temperature of 383 K, 5 gm of catalyst loading, and stirrer speed 100 rpm. The resultant results are shown in Figure 4.

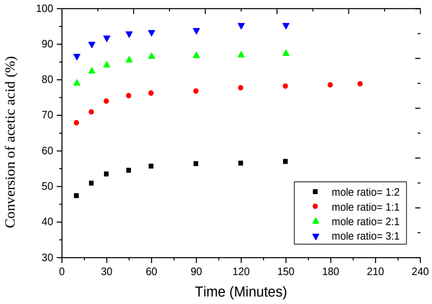

Figure 4 Effect of mole ratio on acetic acid Conversion

Temperature =383K, Stirrer Speed: 1000 rpm, Catalyst loading =5 gm, Catalyst: TULSION MP T-63, Particle size= 0.2 mm-1.3mm

As observed, the equilibrium conversion increases with the initial iso-amyl alcohol-to-acetic acid mole ratio under otherwise identical conditions. The equilibrium conversion of acetic acid increased from about 52% at a feed mole ratio (alcohol to acid) of 1:1 to 92.1% at a feed mole ratio (alcohol to acid) of 3:1.

4.4 Effect of Temperature

The study on the effect of temperature is extremely imperative for a heterogeneously catalyzed reaction, as this information is helpful in calculating the activation energy for this reaction. Moreover, the intrinsic rate constants are strong functions of temperatures. Figure 5 presents the variation of conversion of acetic acid at different reaction temperatures in the range 363 K to 403 K at a feed mole ratio (alcohol to acid) of 1:1, at a stirrer speed of 1000 rpm, and at 5 gm of catalyst loading. It shows that the higher temperature yields the greater conversion of acetic acid at a fixed contact time under otherwise identical conditions. Increasing the temperature is apparently favorable for the acceleration of the forward reaction. However, the equilibrium conversions are nearly equal. (about 90%) The equilibrium conversion of acetic acid is independent of catalyst loading (after 3 h of reaction).

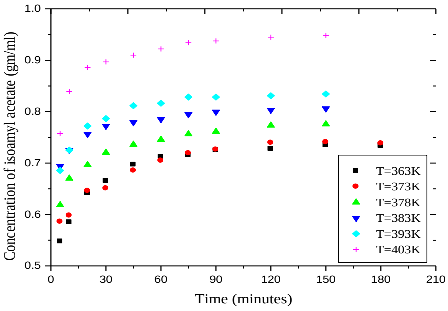

Figure 5 Effect of temperature on iso-amyl acetate concentration

Catalyst loading: 5 gm, Mole ratio= 1:1, Stirrer Speed: 1000 rpm, Catalyst: TULSION MP T-63, Particle size= 0.3-1.2 mm

4.5 Catalyst Reusability

Reusability of TULSION MP-T-63 is determined by performing two runs as given in Table 2. Figure 6 shows effect of catalyst reusability on conversion of acetic acid. After completion of the experiment, the catalyst is filtered, washed with of acetic acid and dried at 110 ^{0}C for 3h. It is observed that the there was only a marginal decrease in conversion. Thus the catalyst is reusable. Hence, we can say that catalyst the can be used repeatedly for this reaction without sacrificing catalytic activity.

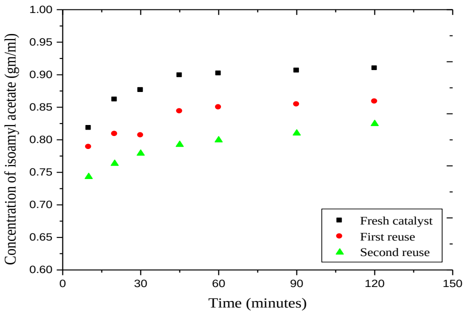

Figure 6 Effect of catalyst reusability (T-63) on concentration of iso-amyl acetate

Stirrer Speed: 1000 rpm, Mole ratio= 2:1, Catalyst Loading: 5 gm, Temperature: 383K, Catalyst: TULSION MP T-63

Table 2 Reusability of the Catalyst (T-63)

Run #	Conversion of Acetic acid (%)
Fresh	89.65
First Reuse	85.20
Second Reuse	79.29

4.6. Kinetic Model fitting using Experimental Data:

The esterification reaction was kinetically controlled since the external mass transfer resistance and the intraparticle diffusion were not present. The catalyst used is a macro porous ion exchange resin. In macro porous resin, the reactants are capable to diffuse into the pores without any resistance (Yadav and Thathagar, 2002). Therefore sorption effects can be neglected and Pseudo-homogenous model should be adequate for the present system. The experimental data collected at temperatures 363 K to 403 K were used to plot –ln (1-X_A) versus time, which is shown in Figure 7. The values of rate constants at different temperatures are calculated. Arrhenius plot (Refer Figure 8) is used to estimate the frequency factor and energy of activation. The values of, -lnk is plotted 1/T as shown in Figure 8.

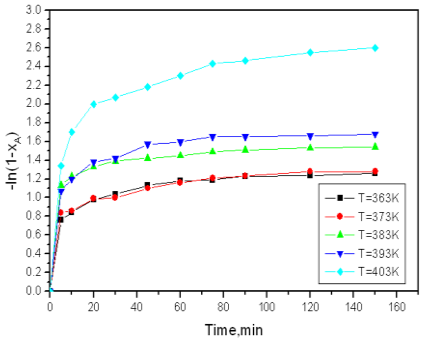

Figure 7 Pseudo first order kinetic plot of esterification of iso-amyl alcohol with acetic acid

The values of frequency factor and the activation energy are calculated as 3.54 x 10^3 moles/gm.min and 41.88 kJ/mol respectively. The kinetic expression for iso amyl acetate synthesis over ion exchange resin (T-63) is given by:

$$k_1 = 3.54 \times 10^3 \exp\left(\frac{-41.88}{RT}\right) \qquad [13]$$

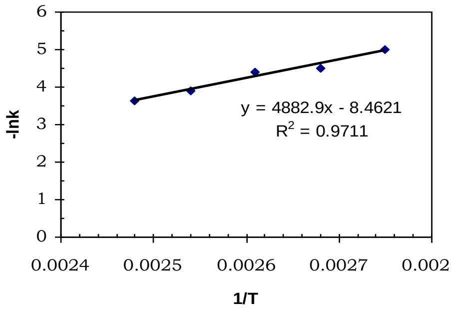

Figure 8 Arrhenius plot for esterification of iso-amyl alcohol with acetic acid

This high value of activation energy also confirmed that the overall rate of reaction is not influenced by either external mass transfer or intraparticle diffusion resistance and it is an intrinsically kinetically controlled reaction on active sites.

Conclusions

The esterification reaction between 1-Pentanol and acetic acid is studied over an acidic ion exchange resin (TULSION T-63, MP). Reliable kinetic data and a model covering a wide range of operating conditions are presented with the parameters. The interaction between the solid catalyst and the reactants are considered in the model. The resulting model and parameters estimated can easily be included in the simulation of RD columns. A kinetic model is built up which recommended that the reaction is intrinsically kinetically controlled. The apparent activation energy is 41.88 kJ/kmol.

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Nomenclature

A = iso-amyl alcohol
[A0] = Concentration of A in bulk liquid phase, mol/cm^3
[As] = Concentration of A at the solid (catalyst) , surface, mol/ cm^3
B = Acetic acid
b = Stoichiometric coefficient
[B0] = Concentration of B at the solid (catalyst) , surface, mol/ cm^3
[Bs] = Concentration of B in bulk liquid phase, mol/cm^3
C = iso-amyl acetate
D = Water
a_p = Solid-liquid interfacial area, cm^2/cm^3

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Table 1 Properties Catalyst used (Thermax India Ltd.), [14]

Catalyst	Particle Size (μm)	Exchange capacity (meq/dry g)	Bulk density (kg/m^3)	Moisture content (%)	Porosity (%)	Temp. stability (K)	Specific surface area (m^2/gm)	Pore Dia. (A)	Cross linking (%)
T-62	300-1200	4.8	NA	<1	NA	403	35	NA	15
T-63	300-1200	4.9	NA	<1	40	408	35	400	15
T-66	300-1200	5.0	NA	<1	NA	403	NA	NA	NA