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ISOMERIZATION OF α- PINENE TO CAMPHENE

MASTER OF SCIENCE

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PREFACE

In this study isomerization reaction of α-pinene was studied. Selectivity, reaction parameters and kinetics of the reaction were investigated.

I would like to thank Proffesor Doctor Gönül Gündüz for supervising this study, for her valuable suggestions, critisms, encouragement and support in the preparation of this project.

I also would like to thank Aldrich Company for the supply of camphene, Ortas/Edremit Wood Turpentine Company for the supply of turpentine, Prof.Dr. Sümer Peker for the supply of clays and her valuable helps in the optimization study, Prof.Dr. Semra Ulkü for the supply of clinoptilolite, Prof.Dr. Mithat Yüksel for the use of high pressure reactor, Ilhami Taskiran for his valuable helps in gas chromotographic analysis, Mehmet Akcay for his valuable helps in atomic absorption analysis and Department of Mining Engineering for the sieve analysis.

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ABSTRACT

Production of camphene from α-pinene was studied in this study. Different catalysts were tested and the most selective catalyst was found as clinoptilolite which was a natural zeolite. The effects of the reaction parameters such as temperature, catalyst amount, time, particle size, agitation on the yield of camphene were investigated. The yield of camphene at the optimum conditions is 42.84 %. And the kinetics of the reaction was also studied.

1. INTRODUCTION

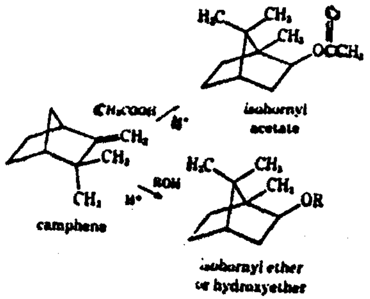
1.1. The Purpose of the Study

The purpose of the study was to investigate the isomerization of α-pinene to camphene over several catalysts in a batch slurry reactor, to determine the most selective catalyst for the camphene production and to establish a relationship between the yield of camphene and the α-pinene/catalyst ratio, the temperature and the reaction time from a statistical analysis of a set of experiments according to a central composite design. In addition, it was tried to determine the kinetics of the isomerization of α-pinene to camphene over the most selective catalyst.

1.2. The Importance of Camphene

As known, camphene is an important chemical of industry from which many products of commerce are made. In general camphene is consumed in the production of toxaphane, isobornyl acetate, isoborneol and camphor. Comparatively small amounts are used in producing fragrance chemicals by reaction with phenols; typically such compounds have woody odors.

Toxaphene, a potent insecticide that is especially effective against the cotton boll weevil, is produced in tonnage quantities yearly by chlorination of camphene. When camphene reacts with acetic acid in the presence of a strong acid catalyst, isobornyl acetate is produced. Acid catalyzed reaction of camphene with alcohols or glycols produces isobornyl ethers or hydroxyethers, which are notable for their woody, cedar like odors, as presented below:



R = alkyl or hydroxyalkyl

1.3. Production of Camphene

Camphene is produced commercially by treatment of α-pinene over acidic catalysts in the absence of water. It can be produced similarly from β-pinene, pinene containing materials such as gum turpentine, wood turpentine and sulfate turpentine which is obtained in the manufacture of paper from delignification of wood. Production from β-pinene is more expensive. Tricylene is always obtained with camphene as an equilibrium product. The isomerisation of α-pinene is generally carried out at reflux temperature in the presence of titania, minerals containing the specific group of silicates or activated clays.Preparation of the catalyst has a great influence on product yield and composition. Many other diverse acidic catalysts have been evaluated but apparently have not achieved commercial importance. The chief by-products of the isomerization are p-menthadienes, which are collectively referred to as dipentene in the trade These are removed from the camphene-tricyclene product by fractional distillation and then the camphene-tricyclene is distilled at reduced pressure to produce cuts containing varying amounts of two products which are blended to suit the intended end use. Commercial camphene contains a camphene:tricyclene ratio 4:1 and has a minimum melting point of 39-46 °C. In most applications, tricyclene undergoes the same chemical reactions as camphene. One of the main products of the isomerization of α-pinene is limonene. The most important terpene resins are those made from limonene or dipentene, β-pinene and α-pinene via cationic polymerization. Optically active d-limonene is a by-product of the citrus fruit industry. dl-Limonene is sometimes used to designate a crude distillate fraction from pull mill liquor. dl-Limonene in addition to other terpenes formed in the processing of sulfate liquor from craft paper manufacture (1).

Table 1 presents some physical proporties of α-pinene, camphene and limonene.

Table 1. Some physical properties of α-pinene, camphene and limonene

Common name	Bp,°C	Mp,°C	d,g/cm^3	n_d	$(\alpha)_d$
α-pinene	156	-50	0.8595	1.4658	±51
camphene	158	49			±108
limonene	176.5	-74	0.841	1.4730	±124

1.4.The Literature on the Production of Camphene

Many methods have been suggested in the literature for the preparation of camphene. One of them is the production of camphene from bornyl chloride attempting to produce a chlorine free product.Attemps to produce chlorine-free camphene have led to the development of various one-step methods using a catalyst to promote the isomerization of pinene directly to camphene, thus eliminating the bornyl chloride stage.Several methods have been reported using various types of catalysts both organic and inorganic as well as mineral to effect this one step conversion of pinene directly to camphene.In all cases, where organic or inorganic type catalyst are used,the yield of desirable products has been relatively low as, for example, in the neighborhood of about 15 % .The catalysts, in most cases,must be treated by means of an acid to activate the surface there of. This activation improves the behaviour of the catalyst so that yields of camphene as high as 50 % are realized .However, these relatively higher yields are obtained only after the pinene being isomerized has been subjected to prolonged heating periods in the presence of the catalyst (2).

Carson has discovered a new catalytic process where in it has been found that the specific group of silicates known as the chlorites would promote the isomerization of isomerizable terpenes giving relatively high yields of pure camphene in a relatively short period of time.

The chlorites are silicates of magnesium or iron, usually occuring in scally aggregetes and being softer than the micas and pliable instead of being elastic. According to Pauling, chlorite structure consists of alternate micalike and brucite-like layers. The mica-like layers have a composition varying between $\mathrm{Mg_3(AlSiO_{10})(OH)_2}$ and $\mathrm{Mg_2Al(Al_2Si_2O_{10})(OH)_2}$ and the brucite-like layers have the composition $\mathrm{Mg_2Al(OH)_6}$. Each of the specific minerals that may be grouped and referred to as chlorites and known by the mineral names, prochlorites, clinochlore and pennite, may be represented by a type structural formula varying from $\mathrm{[O_6{\cdot}AlSi_3O_4(OH)_2Mg_6(OH)_2O_4AlSi_3O_6][(OH)_6Al_2Mg_4(OH)_6]}$ to $\mathrm{[O_6Al_2Si_2.O_4(OH)_2.Al_2Mg_6.(OH)_2O_4.Al_2Si_2O_6][(OH)_6.Al_2Mg_4(OH)_6]}$. According to Carson, a quantity of a chlorite mineral is dried for one hour at 100 °C and pulverized to a grain size of about 28 mesh. One part of this mineral catalyst is slowly added to 43 parts of α-pinene which is held at the reflux temperature until addition of the catalyst was complete. The mixture is refluxed for two hours during which time the temperature of the reaction mixture has risen from 156 to 165 °C. And then the mixture is cooled, filtered to remove the catalyst and filtrate is fractionated. It was found that a 90 % conversion of the pinene was obtained at the given temperature in 10 minutes to give a yield of 63 % (weight) solid camphene, based on total pinene used, the remainder of the material being chiefly monocyclic terpenes. Although the reaction rate increases in fineness of the catalyst, little effect of fineness has been noticed above a grain size of about 0.075 mm. The prefferred operating range is between about 155 °C and 167 °C at normal atmospheric pressure. It is reported that under proper conditions of pressure, temperatures up to 200 °C or higher may be used. At atmospheric pressure, the reaction time may vary between about 10 minutes and about 8 hours.Completeness of isomerization of pinene is desirable. When the reaction is not carried to completeness, unreacted terpenes as, for example α-pinene remain in small percentages and because of the relative closeness of the boiling points of α-pinene and camphene, seperation by the ordinary methods of fractional distillation is not feasible.

The ratio of chlorite catalyst used to the terpene being treated may vary between about 0.005 and 0.1 and is preferably between 0.015 and 0.025.

Kirkpatrick (3) used halloysite as catalyst for the isomerization of pinene to camphene. Halloysite is an aluminium silicate mineral having a chemical formula approximating $Al_2O_3.2SiO_2.2H_2O$. Its crystal structure consists essentially of an irregular or disorderly stacking of layers which may be represented by the general type structural formula $O_6.Si_4.O_4(OH)_2Al_4(OH)_6$. They reduced a quantity of 0.147 mm -0.075 mm and washed it with a relatively weak solution of acetic acid and then washed it distilled water and then heated at 250 °C for one hour. Later, one part of this treated halloysite was added to 25 parts of commercial α-pinene containing about 96-97 % α-pinene and mixture was heated to a temperature of 150 °C. After 10 minutes of heating the reflux temperature was 170 °C. It was found that a 90 % conversion of the pinene was obtained at the given temperature in 10 minutes to give a yield of 60 % camphene. The time for complete conversion of the terpene being isomerized varies with the amount of catalyst used and the temperature employed.The ratio of catalyst to the terpene being treated may vary between about 0.01 and 0.1 and is preferably between 0.03 and 0.04 .

In one study (4), the gas-liquid chromotographic analysis of the isomerization products of α-pinene was studied to seperate them with a high accuracy.

Korotov and coworkers (5) prepared camphene by isomerization of pinene in the presence of TiO_2. Pinene vapors in an inert gas were passed through a layer of Ti catalyst suspension in camphene at a flow rate of 9ml/s. They obtained a product containing 96 % camphene.

Petelina and coworkers (6) studied the seperation of the main products such as camphene and tricyclene of the isomerisation of α-pinene by means of a cation exchance capacity and the swelling ability of Ankalite KT-3 on the composition of the product of the catalytic isomerization of α-pinene. They prepared various samples of Alkalite KT-3 changing the ratio and order of addition of the reactants and the temperature of condensation.They found that the yield of the camphene and tricyclene increased as the swelling ability of the resin increased and as the exchance capacity decreased. The maximum yield of camphene was obtained to be 47.7 % and of tricyclene 9.3 % .

Afanas'eva and coworkers (7) studied the continuous isomerization of technical pinene into camphene under laboratory conditions. Pinene vapor diluted with nitrogen was bubbled through the heated of a Ti catalyst in camphene (first pass) or in the isomerisation mixture (subsequent passes). After three passes, isomerization of pinene gave a product containing 96 % camphene. The effects of several parameters such as vapor feed rate, temperature and α-pinene concentration in the feed on the production of camphene were investigated.

Later on, the same investigators (8) used a pilot plant for the continuous isomerization of α-pinene into camphene. The pilot plant was a vertical column through which a liquid suspension of a Ti catalyst in camphene flowed downwards, while α-pinene vapor moved upwards. A product consisting typically of 80.1 % camphene, 14.5 % tricyclene and other terpenes was produced from a feed stock containing 82 % α-pinene. The overall yields of camphene and tricyclene was found to be about 50 % on feed without recycling.

In a Japan patent (9) isomerization of pinene to camphene using TiO_2-$Ti(OH)_4$ catalyst was described. According to the patent, the titanium catalyst used was prepared as follows: 1 mole of TiO_2 in 25 % aqueous solution of NaOH is heated 6 hours at 120 °C, the precipitate was washed with water, acetic acid was added (to pH 2.4-2.6), the precipitate was again washed with water and the pH adjusted to 3-3.5 to give a catalyst. 100 parts of pinene were heated 2 hours with 2 parts catalyst at 145 °C and filtered to give an oil containing 65 % camphene.

In one study (10) activated carbon has been used as catalyst to produce camphene. The experiments showed that activated carbon increased the yield of camphene while decreasing polymer formation during the isomerization of a pinene containing feed. In that study, 100 parts of α-pinene were mixed with 2 parts of a commercially available activated carbon under the trade name Darco S-51. The mixture was agitated while passing a stream of nitrogen over the surface of the mixture to provide an inert atmosphere.The contents were next heated for about two and one half hours at reflux temperatures ranging from 156 °C to 165 °C. After cooling the reaction mixture, it was filtered and the catalyst was removed. From the analysis of filtrate a yield of camphene based on the weight of reacted α-pinene was found to be 58.8 % .When the activated carbon was dried in oven at 200 °C for twelve hours prior to use and the mixture was heated at reflux 156°C increasing to 165 °C for one hour, the analysis of the product gave a yield of camphene 59.8 % which was very close to the result obtained before. The amount of activated carbon employed can be varied from 0.5 % to 10 % based on the weight of the material to be treated for good conversions to camphene at temperatures ranging from 75 °C to 175 °C or higher for from about 10 minutes to fifteen hours. The mixture obtained is rich in camphene, free of polymers and low in by-product terpene formation.

In one work (11), China and fire clays were used as catalysts for the isomerization of α-pinene to camphene. The best yields were obtained with 2 % China clay treated with H_2SO_4 and activated at 350 °C.

Bardyshev and coworkers (12) investigated the chemical reactions of pinenes in the presence of salicyclic acid. Heating α or β pinene with salicyclic acid for 2-360 minutes at 140 °C gave a mixture of products containing camphene, tricyclene, α and γ-fenchene, dipentene, terpinolene, α-terpinen, borneol, isoborneol, α and β fenchol, α-terpineol and polymeric terpenes.

Popov and Vyrodov (13) investigated the isomerization of pinenes containing 92.1 % α-pinene, 1.8 % β-pinene, 4.8% camphene and 1.3 % Δ^3-carene at

110 °C in the presence of activated titanium dioxide. The yield of camphene and tricyclene were found to be 76.2 % and 14.2 % respectively. Increasing the temperature to 130 °C and later to 150 °C decreased the total yield from 92.1 to 85.1 % and to 82.7 %, respectively.

Kullaj (14) studied the isomerization of α-pinene into camphene and tricyclene with different samples of Albanian clay activated by 10 % HCl. Albanian clays were divided into four groups according to the rate of the isomerization of α-pinene into camphene. It was found that, when the isomerization of α-pinene was complete, the isomerization products contained 30 % camphene and 10 % tricyclene independently of the type of activated clay which was used as catalyst.

In another work (15), the relationship between the characteristics such as pH, specific surface area of 10% HCl activated clays and the rate of the isomerization of α-pinene into camphene and tricyclene was investigated but it couldn't be possible to relate them. However, it was observed that the maximum rate of isomerization of α-pinene to camphene was obtained when the SiO_2/Al_2O_3 mol ratio was equal to 5.6 .

In one work (16), it was found that selectivity on an industrial titanium catalyst for isomerization of α-pinene into camphene increased with the amount of Na_2O on its surface, whereas catalytic activity of the sample decreased with increasing Na_2O loading and catalysts containing 1.6 % Na_2O gave 87 % yields of desired products.

Ozek (17) studied the production of odorous compounds from the natural monoterpenes. He obtained a 55 % conversion from the isomerization of α-pinene to camphene over titanium catalyst in 45 minutes and he also studied the effects of several parameters such as temperature, type and amount of catalyst and agitation on the camphene production. In the experiments, he used wood turpentine obtained from Ortas/Edremit. Figure 1 and Table 2 present the gas chromotographic analysis of the turpentine used in that work.

As understood from the literature, there are several studies on the selective catalysts for the isomerization of α-pinene to camphene. But, these studies, in general describe the invention of a new catalyst for the production of camphene from α-pinene. But the statistical analysis of the process, the investigation of the kinetic parameters and reaction kinetics are lacking. The purpose of the present study is to try for determining the relationship between the yield of camphene and three variables, namely, the α-pinene /catalyst ratio, the temperature and the time and also to investigate the kinetic parameters, the kinetics of the isomerization reaction of α-pinene to camphene over the most selective catalyst found.

The study was carried out in three parts. In the first part, the most selective catalyst was determined after a selectivity study made on different eleven catalysts. In the second part of the study, a set of experiments according to an orthogonal central composite design was carried out in order to determine the relationship mentioned above. Finally, the reaction kinetics and kinetic parameters were investigated.

Wood turpentine obtained from ORTAS Turpentine Company/Edremit was used in the experiments. The contents of α-pinene and camphene of the turpentine were determined by gas chromatographic analysis before the runs.

GC analyse condition (17):

system:Shimadzu GC-9A and C-R4A Integrator

column:Thermon 600T (50 m,0.25mm) FFS capiller column

carrier gas:nitrogen

temperature program:70°C in 10 min.,increasing at a rate of 2 °C/min until 180 °C

split ratio: 60:1

dedector temperature:250 °C

injection temperature:250 °C

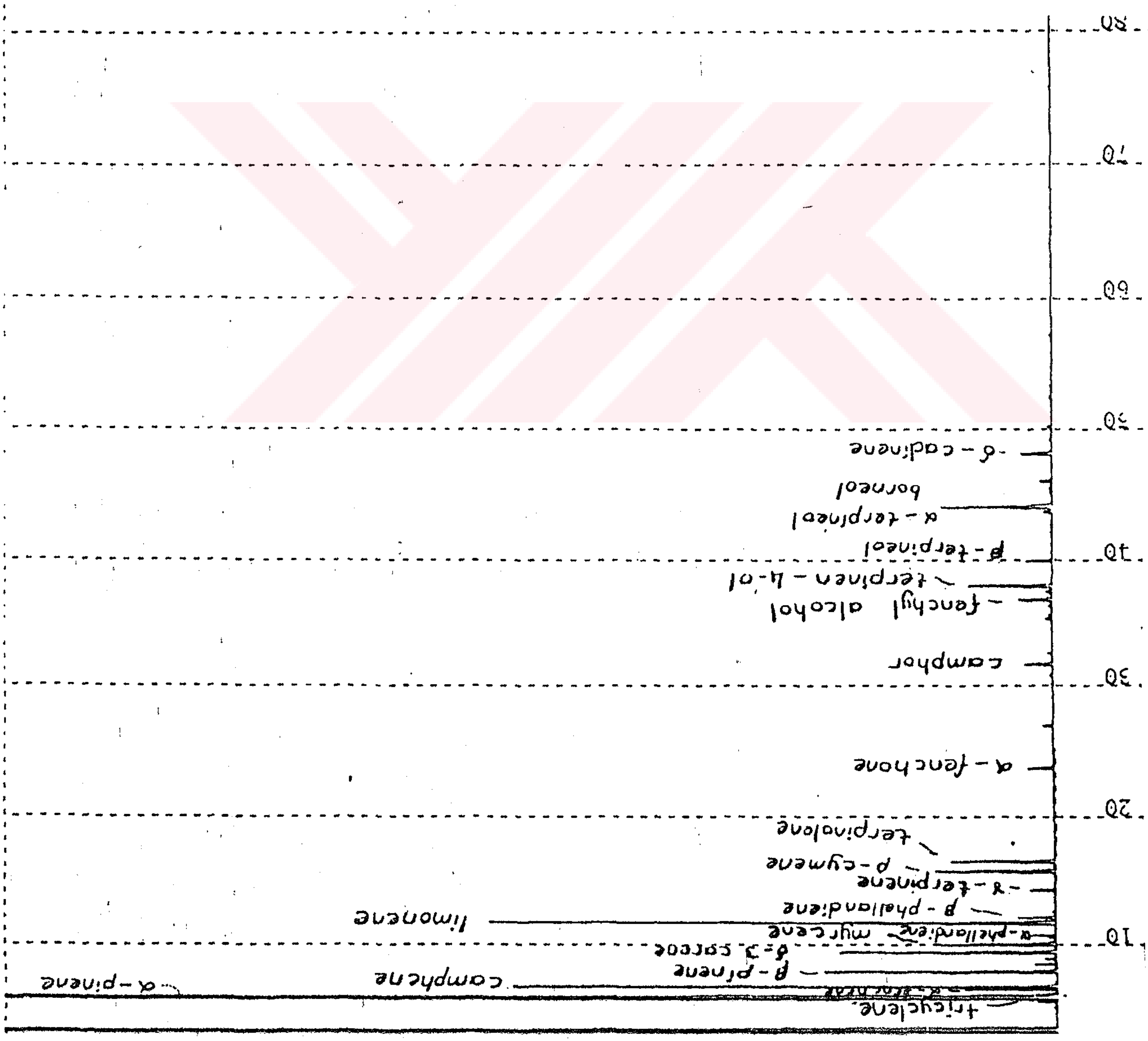


Fig.1. Gas chromatographic analysis of wood turpentine (17)

Table 2 Results of the GC analysis of wood turpentine (17)

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	14	5.17	110	30	V		0.0216	
	17	5.633	660	147	V		0.1289	tricyclene
	18	6.017	403717	58053	SV		78.8347	α-pinene
	20	6.618	2304	655	T		0.4498	α-fenchene
	21	6.825	14265	4078	TV		2.7855	camphene
	22	7.178	79	19	TV		0.0155	
	25	7.95	7385	1690	TV		1.4422	β-pinene
	26	8.33	58	10	TV		0.0113	
	27	8.496	773	166	TV		0.1509	
	28	8.895	410	80	TV		0.08	
	30	9.415	8253	1610	TV		1.6115	δ-3 corene
	31	10.015	5570	878	T		1.0876	mycrene
	32	10.606	343	57	TV		0.067	α-phellandiene
	33	10.78	1071	186	TV		0.2091	α-terpinene
	35	11.791	27667	4270	TV		5.4026	limonene
	36	12.197	1728	279	TV		0.3375	β-phellandiene
	37	12.629	123	20	TV		0.024	
	40	14.323	1231	192			0.2404	γ-terpinene
	41	15.789	5789	913			1.1305	p-cymene
	43	16.596	5052	786	V		0.9864	terpinolene
	46	18.783	51	7			0.01	
	49	23.738	1491	199			0.2911	α-fenchone
	52	26.971	567	81			0.1106	
	53	30.163	91	11			0.0178	
	55	30.767	275	24	V		0.0537	
	56	31.684	1677	209			0.3274	camphor
	57	32.587	248	39			0.0484	
	59	35.318	364	49			0.071	
	60	35.61	257	30	V		0.0501	
	62	36.317	195	19	V		0.038	
	64	36.828	1789	255	V		0.3494	fenchyl alcohol
	66	37.455	324	44	V		0.0632	
	67	37.633	75	9	V		0.0147	
	68	37.962	4362	637	V		0.8517	terpinen-4-ol
	72	39.958	1335	196	V		0.2606	β-terpineol
	75	41.308	77	10	V		0.015	
	77	41.975	60	7			0.0118	
	78	42.217	103	11	V		0.02	
	80	42.717	73	10	V		0.0143	
	81	42.85	107	12	V		0.021	
	82	43.145	109	16	V		0.0213	
	84	43.81	549	64			0.1072	α-terpineol
	85	44.183	7075	835	V		1.3815	borneol
	87	45.339	112	15	V		0.0218	
	88	45.55	206	21	V		0.0401	
	90	46.12	738	91	V		0.1442	
	91	48.184	1948	234			0.3804	δ-cadinene
	93	49.194	111	12			0.0216	
	94	49.567	83	10	V		0.0162	
	96	50.196	333	39	V		0.065	
	97	52.433	86	11			0.0168	
	98	52.55	108	14	V		0.0212	
	99	53.413	93	14			0.0181	
	107	57.3	152	19	V		0.0296	
	112	65.4	53	3	V		0.0103	
	113	66.25	62	8			0.0121	
	114	66.783	106	12	V		0.0206	
	120	75.575	77	7			0.0151	
	TOTAL		512106	77401			99.9999	

1.5. Kinetic Analysis

1.5.1. The Effect of Physical Processes on Observed Rate of Heterogeneous Catalytic Reactions

For an irreversible fluid phase reaction on a solid catalyst pellet, the diffusion rate from the bulk fluid to the surface can be expressed as follows:

$$r_p = k_m a_m (c_b - c_s) \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

where c_b and c_s are the concentrations of the reactant in the bulk fluid and at the surface respectively. k_m is the mass transfer coefficient between bulk fluid and solid surface and a_m is the external surface area per unit mass of the pellet.

The rate of the reaction on the surface, for a first order reaction,

$$r_p = k\, c_s \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

When both diffusion and reaction resistance are significant, and for a first order reaction, at steady state Eqs.(1) and (2) can be solved for the unknown surface concentration. This result for c_s can be substituted in Eq.1 to obtain an expression for the rate in terms of the bulk concentration c_b. If this is done, the results below are obtained:

$$c_s = \frac{k_m a_m}{k + k_m a_m} c_b \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$r_p = k_o\, c_b = \frac{1}{1/k + 1/k_m a_m} c_b \quad \ldots\ldots \quad (4)$$

where $$\frac{1}{k_o} = \frac{1}{k} + \frac{1}{k_m a_m} \quad \ldots\ldots \quad (5)$$

Eq.(4) shows that for the intermediate case the observed rate is a function of both the rate of reaction constant k and the mass-transfer coefficient k_m. Eq.(5) can be written as:

$$\frac{1}{k_o} = \frac{1}{k} + \frac{1}{k_m a_m} = \frac{e^{+E/RT}}{A} + \frac{1}{k_m a_m}$$

$$\text{or} \quad k_o = \frac{A k_m a_m e^{-E/RT}}{k_m a_m + A e^{-E/RT}} \quad \ldots\ldots (6)$$

where $Ae^{-E/RT}$ has been substituted for the rate constant k of the surface step. Here E is the true activation energy of the surface reaction. Since the mass transfer coefficient is relatively insensitive to temperature, Eq.(6) shows that k_o approaches a nearly constant value equal to $k_m a_m$ at high temperatures. At low temperatures $k_o \cong Ae^{-E/RT}$, since $k_m a_m$ is the dominant term in the denominator, and a straight line is obtained on the Arrhenius plot. Figure 2 illustrates these results. At low temperatures the slope of the straight line gives the correct activation energy, E, of the surface reaction. As the temperature increases, a curve which ultimately flattens to a nearly horizontal line is obtained. In this region E' would vary with the temperature. When experimental rate data for fluid-solid catalytic reactions show a curved line as in Fig.2 ,it is possible that the external diffusion resistances are important.

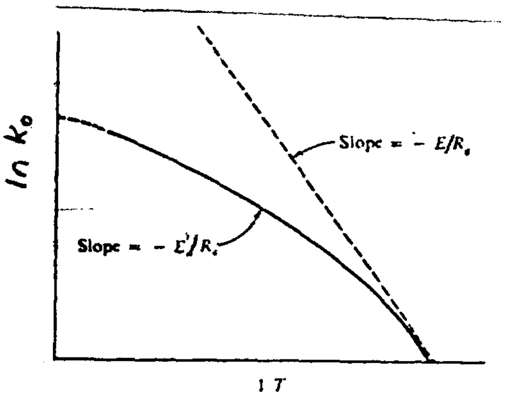


Fig. 2. True (E) and apparent (E') activation energies

Under the isothermal conditions, the bulk fluid temperature is equal to the surface temperature of the solid catalyst. Hence, temperature diferences due to the external heat transfer resistance are not considered.

On the other hand, it is well known that the internal mass transfer resistances can be eliminated by decreasing the size of the catalyst particles, increasing the effectiveness factor (18).

1.5.2. Effects of External Diffusion Resistance on Selectivity

When more than one reaction occurs, the effect of external transport on selectivity is important. The local or point selectivity, S_p, at any location in a reactor is defined as the ratio of the rates of the desirable to the undesirable product. Consider a first order parellel reaction for isothermal condition:

$$A \xrightarrow{k_1} B \quad \text{desired}$$

$$A \xrightarrow{k_2} C$$

where B is the desired product. The selectivity of B with respect to C is given by the ratio of the rates

$$S_p = \frac{r_B}{r_C} = \frac{k_1(C_A)_s}{k_2(C_A)_s} = \frac{k_1}{k_2} \quad \ldots. \; (7)$$

Regardless of how much the surface concentration is reduced by mass transfer, Eq. 7 shows that the selectivity is unaffected. For this type of parellel reactions the rate is reduced by mass transfer but the selectivity is unchanged. Eq. 7 is applicable when external temperature differences are significant, but the rate constants k_1 and k_2 must be evaluated at the surface temperature. The effect of heat transfer on selectivity depends on the activation energies of the reactions. Eq. (7) gives

$$S_p = \frac{A_1 e^{-E_1/RT_s}}{A_2 e^{-E_2/RT_s}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \; (8)$$

If there were no heat transfer resistance $T_s = T_b$. Hence the ratio of selectivities with and without considering external temperature differences would be

$$\frac{(S_p)_{T_s}}{(S_p)_{T_b}} = \frac{\exp[(E_1/R)((T_s - T_b)/(T_s T_b))]}{\exp[(E_2/R)((T_s - T_b)/(T_s T_b))]} \qquad (9)$$

When the net heat of reactions is exothermic, $T_s - T_b$ is positive. Hence if $E_1 > E_2$, the selectivity at T_s will be greater than that at T_b. That is, the selectivity is increased by mass transfer resistances for an exothermic reaction when the activation, E_1, for the desired reaction is larger than E_2 for the by-product reaction. For a net endothermic heat effect the effect of heat transfer would be to reduce the selectivity when $E_1 > E_2$.

1.5.3. Kinetics of Parellel Reactions

The rate of a heterogeneously catalyzed liquid phase reaction per unit mass of catalyst can be given by the following equation:

$$-\frac{V_l}{M_c}\frac{dC_{A_s}}{dt} = k_1 (C_A)_s \quad \ldots\ldots\ldots\ldots\ldots \quad (10)$$

where M_c= weight of catalyst (g), V_l= volume of the liquid (cm^3), k_1= reaction rate constant, C_{A_s}=surface concentration of reactant A.

If the external diffusion resistances are neglected, surface concentration become equal to the bulk concentrations. So, Eq. (10) can be written in terms of the bulk concentrations, that is, in terms of C_A instead of $(C_A)_s$.

For a first order parellel reaction system catalyzed by solid in liquid phase

$$\begin{array}{l} A \xrightarrow{k_1} B \quad \text{desired} \\ \searrow_{k_2} \; C \end{array}$$

$$-\frac{V_l}{M_c}\frac{dC_A}{dt} = (k_1 + k_2) C_A \quad \ldots\ldots\ldots\ldots \quad (11)$$

$$\frac{V_l}{M_c}\frac{dC_B}{dt} = k_1 \; C_A \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

$$\frac{V_l}{M_c}\frac{dC_C}{dt} = k_2 \; C_A \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

If the Eq. (11) is integrated, following equation is obtained:

$$-\ln C_A/C_{A_0} = (k_1 + k_2)\,\frac{M_c}{V_1}\,t \quad \ldots\ldots\ldots \quad (14)$$

Eq.(14) shows a linear relation between $-\ln(C_A/C_{A_0})$ and t . So (k_1+k_2) value is obtained from the slope of the line.

To eliminate time in Eqs. (12) and (13) these equations are divided by Eq. (11) .

$$\frac{dC_B}{dC_A} = -\frac{k_1}{k_1+k_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

$$\frac{dC_C}{dC_A} = -\frac{k_2}{k_1+k_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

Eqs.(15) and (16) are integrated with the conditions that $t=0$, $C_A=C_{A_0}$, $C_B=C_{B_0}$, $C_C=C_{C_0}$ then the yields of B and C are:

$$X_B = \frac{C_B - C_{B_0}}{C_{A_0}} = \frac{k_1}{k_1+k_2}\left(1-\frac{C_A}{C_{A_0}}\right) = \frac{k_1}{k_1+k_2}\,X_t \quad (17)$$

$$X_C = \frac{C_C - C_{C_0}}{C_{A_0}} = \frac{k_2}{k_1+k_2}\left(1-\frac{C_A}{C_{A_0}}\right) = \frac{k_2}{k_1+k_2}\,X_t \quad (18)$$

where X_t is the total conversion. The ratio of Eq. (17) to (18) gives

$$\frac{X_B}{X_C} = \frac{k_1}{k_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$$

In similar way, the ratio of the Equations 12 and 13 gives Equation 20.

$$\frac{dC_B}{dC_C} = \frac{k_1}{k_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (20)$$

After integration of Eq. 20, Eq.21 which is equal to the ratio of the yield of B to the yield of C is obtained.

$$\frac{C_B - C_{Bo}}{C_C - C_{Co}} = \frac{k_1}{k_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (21)$$

As seen Eq.21 is identical to Eq. 19.

The ratio of k_1 to k_2 is obtained by plotting X_B against X_C. By using Eqs. (14) and (19) rate constants, k_1 and k_2, are calculated seperately.

2. EXPERIMENTAL

2.1. Catalyst Preparation

In selectivity studies for the isomerization of α-pinene to camphene, depending on the information about the catalysts in literature, several materials such as halloysite, activated clay, activated titanium dioxide, titanium oxide/silicagel and natural zeolite (clinoptilolite) have been employed for the preparation of the catalysts. After the selectivity screening test, the most selective catalyst has been determined and later, this selective catalyst has been used in the statistical analysis of the experiments according to a central composite design and used in kinetic studies.

The catalysts used in this work were prepared as follows:

A.Halloysite Catalyst

During the preparation of halloysite type of catalysts, the method described by Kirkpatrick (3) was employed.

1. Halloysite 1

A quantity of halloysite composed of 27 %Al_2O_3,57% SiO_2 and 16 % H_2O is reduced into the powder form by grinding and treated with a weak (14.3 % w) solution of acetic acid for 15 minutes, then it is filtered and washed with distilled water. After this pretreatment, halloysite is again treated with the solution of acetic acid under the continuous stirring for 1 hour. After filtration it is washed with distilled water and heated at 250 °C for one hour.

2. Halloysite 2

To prepare this catalyst, the method in the preparation of Halloysite 1 is used. The only difference is in the treatment time. Halloysite in the desired size is contacted with the acetic acid solution under continuous stirring for two days instead of one hour.

B. Activated Carbon Catalyst

For the preparation of this catalyst, the methods given by Davis (10) and Yolgörmez (19) have been used.

3. Activated Carbon

Activated carbon ground to a grain size of approximately 0.075 mm. is contacted with a HCl solution of 10 % for one night. After filtration, it is washed with distilled water and dried at 105 °C for 2 hours.

C. Activated Clay Catalyst

The clay catalyst were activated by the treatment of clay with HCl solution (11, 14, 15,20)

4. Activated Clay 0

This catalyst is an activated clay obtained from the margarine department of Taris Oil Company in Izmir.

5. Activated Clay 1

This catalyst is also an activated clay, but it is activated by dry method (20) .According to this method, the clay from Madak Company is mixed with a HCl solution until the mixture becomes mud whereby the weight ratio of water to acid is 4 and acid to clay is 0.4 .Theh clay is heated in a 150 °C oven for 4 hours. The product obtained is washed with water and the pH is adjusted to 3-3.5 give a catalyst and then it is dried at 105°C for 4 hours.

6. Activated Clay 2

The clay obtained from Madak Company is activated with the method given in the preparation of activated clay 1 .

7. Activated Clay 3

Green clay obtained from Ankara region is used. The activation procedure described above is repeated.

D.Titanium Catalysts

One of the catalysts used in the isomerization of α-pinene to camphene is titanium catalyst (5, 7, 9, 13, 16, 17) and it was prepared as follows:

8. Titanium dioxide - Silicagel Catalyst

The mixture of titanium dioxide (Sigma) and silicagel (Merck) with a mole ratio of 1/1 is treated with a HCl solution of 9 % for one night. Then the mixture is washed with distilled water and dried at 105°C for 2.5 hours. After drying, the mixture obtained is calcined at 500°C for 4 hours.

9. Titanium dioxide - Sodium hydroxide Catalyst

1 mole TiO_2 in 25 % aqueous solution of NaOH is heated 6 hours at 120 °C, the precipitate is washed with distilled water, acetic acid is added (to pH 2.4-2.6) . The precipitate is again washed with distilled water and the pH is adjusted to 3-3.5 to give a catalyst. The catalyst is dried at 105 °C for 5 hours.

10. Titanium dioxide -Sodium hyroxide -Silicagel Catalyst

Preparation procedure for catalyst 9 is applied to the mixture of titanium dioxide -silicagel with a mole ratio of 1/1 .

E. Natural Zeolite

One of the catalysts tested in the isomerization reaction of α-pinene to camphene is clinoptilolite which is a natural zeolite. According to Bottlova and coworkers (16), Na_2O increases the selectivity of the catalyst (Titanium in that work) into camphene . And it is also known that, in the isomerization of α-pinene oxide, SiO_2-AlO_3 catalysts are preferred (21) . Considering the composition of clinoptilolite which is an alkali and alkali-earth hydro alumina silicate it was decided on trying clinoptilolite as a catalyst.

The zeolite tuffs rich in clinoptilolite obtained from Bigadic (Balikesir) was activated as follows to use it on the isomerization of alpha-pinene to camphene. The tuff samples were also analyzed for their chemical composition by means of atomic absorption spectrometer (Varian 10 Plus) except gravimetrically analysis of SiO_2 and water. The chemical composition found is 74.86 % SiO_2, 0.42 % Fe_2O_3, 0.70 % MgO, 0.50 % Na_2O, 2.71 % K_2O, 9.04 % H_2O, 2.42 %CaO, 9.35 % Al_2O_3.

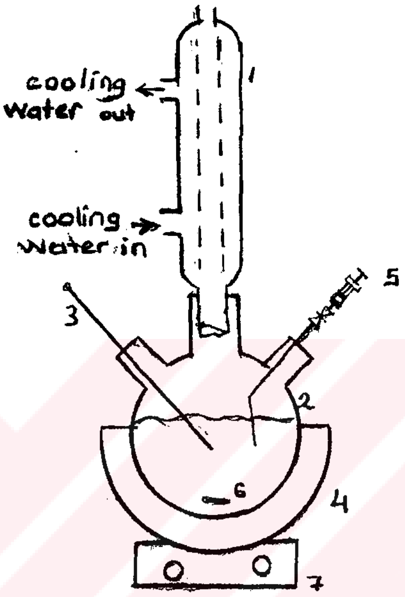
11. Clinoptilolite Catalyst

A quantity of clinoptilolite is contacted with distilled water for 2 hours and then dried at 105°C .It is reduced into the powder form by grinding and then activated at 300°C for 24 hours.

2.2. Experimental Set-up

A schematic diagram of the experimental system used for this study is shown in Figure 3.

The experiments are done in a three-neck, 250 ml. flask. The necks house a sampling syringe, a condenser open to atmosphere and a thermometer measuring the temperature of the reaction mixture. The flask is heated with a heating mantle (Electrothermal) and is stirred magnetically.



1.condenser	5.sampling syringe
2.three neck flask	6.magnetic bar
3.thermometer	7.control table
4.heater	

Fig.3. Experimental Set-up

2.3. Experimental Procedure

For a typical run, a known amount of catalyst and alpha-pinene are charged to the reactor and equilibrated to the reaction temperature. Throughout the run, the temperature is maintained constant within about ±1°C. The mixture is stirred vigorously slurrying the catalyst uniform by throughout the liquid.

Condenser cooling water is started. Represantative samples are withdrawn periodically using a syringe (Birgi) and the catalyst is immediately seperated from the liquid phase by filtration. The sample of liquid phase is analysed by a Hewlett-Packard gas chromatography using flame ionization detector.

A capillary column of HP-FFAP (25mm. long, 0.32 mm diameter) is used with nitrogen flow of 1 ml/min .The temperature of the injection is 270°C. Oven temperature is 60°C. Temperature increases at a rate of 2°C/min until 130°C then increases at a rate of 3°C/min until 215°C. The sample volume is 0.5 µl. Figure 4 shows an example of a GC analysis of a run.

The percentage yield of camphene is calculated from the following equation:

$$Y\% = \frac{\text{weight of camphene obtained}}{\text{wegiht of } \alpha\text{-pinene in the original mateial}} 100 \qquad (22)$$

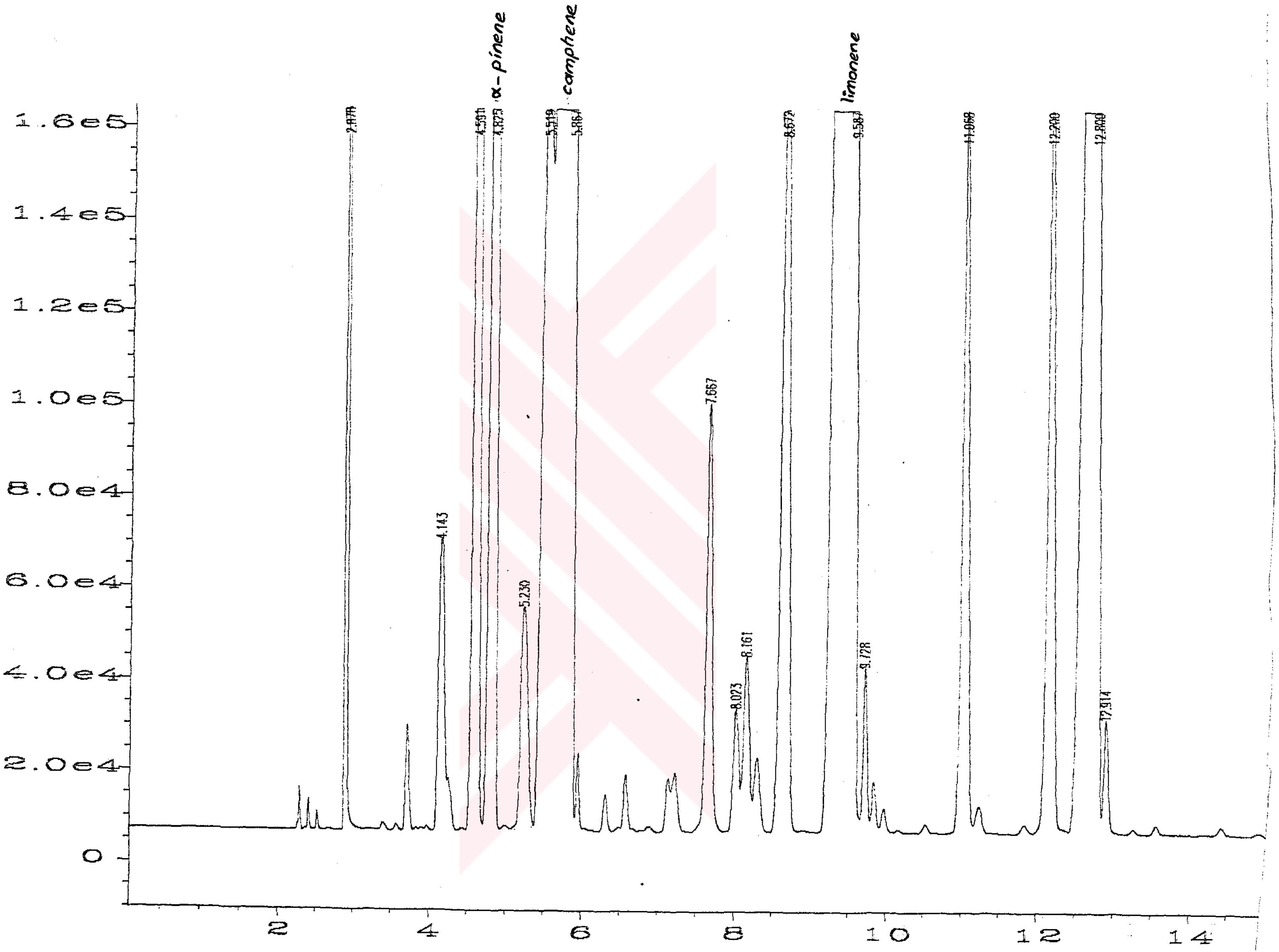


Fig. 4. An example of a GC analysis of a run

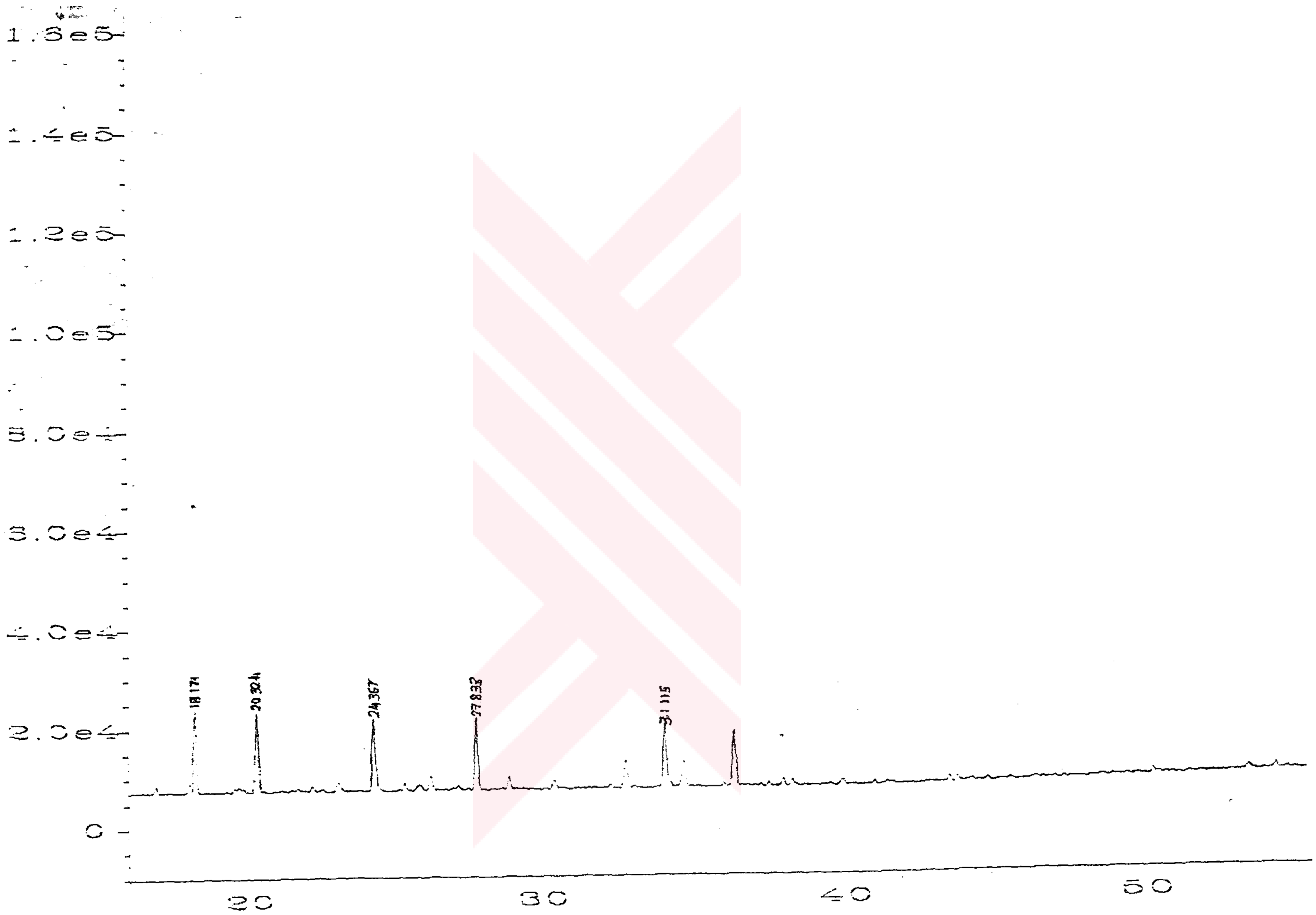


Fig. 4 continued

Table2. Results of the GC analysis of the run in Fig.4

Pk#	Ret Time	Area	Height	Type	Width	Area %	
1	2.878	1234564	859814	BV	0.022	2.5255	
2	4.143	337685	63607	VV	0.084	0.6908	
3	4.591	1932411	408538	VV	0.078	3.9530	tricycle
4	4.825	2959187	643033	VV	0.076	6.0534	α-pinen
5	5.230	332456	49004	VV	0.110	0.6801	
6	5.519	1368707	157951	VV	0.141	2.7999	
7	5.867	1.90152E+007	2104789	VV	0.116	38.8982	camphe
8	7.667	491444	93678	VV	0.082	1.0053	
9	8.023	141253	27024	VV	0.082	0.2890	
10	8.161	212644	38446	VV	0.087	0.4350	
11	8.672	1236695	180507	VV	0.110	2.5298	
12	9.587	1.2173E+007	976919	VV	0.156	24.9016	limone
13	9.728	132646	36175	VV	0.057	0.2713	
14	11.068	878294	163181	VV	0.080	1.7967	
15	12.200	979556	171250	VV	0.088	2.0038	
16	12.800	4816552	479249	VV	0.132	9.8529	
17	12.914	102366	24950	VV	0.063	0.2094	
18	18.174	106368	17082	VV	0.096	0.2176	
19	20.324	106637	16777	PV	0.099	0.2181	
20	24.367	110541	15127	VV	0.114	0.2261	
21	27.833	103444	14944	VV	0.107	0.2116	
22	34.115	112866	13231	VV	0.130	0.2309	

otal area = 4.88845E+007

2.4 Selectivity Experiments and Results of the Experiments

Selectivity experiments were done at the same conditions for all the catalysts. Wood turpentine (Ortas, Edremit) containing 85 % in weight α-pinene was used as a source of α-pinene. 2.5 g. catalyst and 100 g. turpentine were charged to the reactor and heated to the reaction temperature of 155°C . It took about 15 minutes to reach 155°C. The reaction time was taken as 2 hours after reaching that temperature. During the experiments with activated clays the temperature of the isomerization of α-pinene was uncontrollable as mentioned in literature. Temperature increased to 170-180°C in 10-15 minutes and reaction mixture overflowed. That is why, during the runs with activated clays, 1 g. catalyst instead of 2.5 g. was used in selectivity experiments to prevent explosions. It couldn't be possible to operate the reactor at 155°C in the runs with activated clay 3 catalyst. The temperature of the reaction mixture retained constant at 145°C during those experiments.

Due to the difference in the amount of catalyst used, the experiments with activated clay were considered as a different group in comparison with the other catalysts for the selectivity analysis. Each run at the selectivity analysis was repeated 3 times to be able to apply one way analysis of variance.

The results of the selectivity screening test are given in Table 4.The following remarks can be noted from the investigation of the selectivity table.

- To increase the treatment time with acetic acid from one hour to48 hours during the preparation of halloysite catalysts doesn't make any significant difference in the yield of camphene.

- Activated carbon prepared is an unactive catalyst in the production of camphene.

- It is very hard to control the temperature in the runs with activated clay. When the amount of catalyst was decreased from 2.5 g. to 1.0g, the reaction temperature can be maintained at the desired range. Activated clay 2 is more active than the others.

- Titanium catalysts treated with NaOH are not active and selective catalysts prepared by contact with HCl are very selective catalysts in the production of camphene.

- Natural zeolite catalyst in the form of clinoptilolite is the most selective catalyst when it is compared with the other catalysts used in the amounts of 2.5 g. This result was also supported by the calculations of one way analysis of variance (22)

Although the catalyst of activated clay 2 seems to be the most selective one from the point of the amount of catalyst used in the run, we decided on choosing the natural zeolite catalyst (clinoptilolite) as the most selective catalyst due to the reserves of zeolite tuffs rich in clinoptilolite in Bigadic (Balikesir/Turkey). On the other hand, acid clay catalyzed isomerization reactions of α-pinene are rather uncontrollable, leading to severe explosions (10), as also observed in our work. That is why, the other investigations in the present study were done with clinoptilolite catalyst which is choosen as the most selective one.

Table 4. Results of the selectivity screening test

Catalyst type	t(h)	w(g)	T(°C)	%Y
Halloysite 1	2	2.5	155	24.71
Halloysite 1	2	2.5	155	27.63
Halloysite 1	2	2.5	155	28.30
Halloysite 2	2	2.5	155	23.87
Halloysite 2	2	2.5	155	26.92
Halloysite 2	2	2.5	155	31.00
Activated carbon	2	2.5	155	0.90
Activated carbon	2	2.5	155	0.39
Activated carbon	2	2.5	155	3.18
Activated clay 0	0.16	1.5		30.60
Activated clay 0	0.16	1.5		41.13
Activated clay 1	0.16	1.5		31.92
Activated clay 2	0.16	1.5		33.76
TiO_2 - SiO_2	2	2.5	155	42.41
TiO_2 - SiO_2	2	2.5	155	34.57
TiO_2 - SiO_2	2	2.5	155	29.09
TiO_2 - NaOH	2	2.5	155	4.07
TiO_2 - NaOH	2	2.5	155	0.54
TiO_2 - NaOH	2	2.5	155	0.87
TiO_2 - SiO_2-NaOH	2	2.5	155	0.47
TiO_2 - SiO_2-NaOH	2	2.5	155	0.25
TiO_2 - SiO_2-NaOH	2	2.5	155	0.52
Zeolite	2	2.5	155	43.73
Zeolite	2	2.5	155	37.92
Zeolite	2	2.5	155	43.50
Zeolite	2	2.5	155	43.90
Activated clay 0	2	1	155	31.13
Activated clay 0	2	1	155	31.98
Activated clay 0	2	1	155	32.11
Activated clay 1	2	1	155	34.85
Activated clay 1	2	1	155	35.05
Activated clay 1	2	1	155	32.76
Activated clay 2	2	1	155	37.53
Activated clay 2	2	1	155	38.74
Activated clay 2	2	1	155	39.56
Activated clay 3	2	1	145	19.21
Activated clay 3	2	1	145	16.98
Activated clay 3	2	1	145	27.17

2.5. Optimization of the Isomerization of α-pinene to Camphene

Experimental designs are frequently performed in the study of emprical relationships between one or more measured responses and a number of variables. They have been used on a wide variety of problems, for example, in biology, agriculture and chemistry (23).

The responce variable in this study is the percentage yield of camphene defined in Eq. (22). The variables to be considered in the analysis are : the amount of catalyst, the temperature and the time of operation. The amount of α-pinene was not considered as a variable in the analysis, because 100 g. of wood turpentine containing 85 % α-pinene was used as reactant in all the runs.

A central composite rotatable design was used to obtain a relationship between the yield of camphene and catalyst amount, time and temperature.

To assess the effect of each variable they were standardized by defining the dimensionless variable as:

$$X_i = (X_i - X_{io})/\Delta X \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (23)$$

$$\text{That is; } X_1 = \frac{w-5.75}{3.25},\ X_2 = \frac{t-4}{2},\ X_3 = \frac{T-105}{50}$$

(X_1:for amount of catalyst, X_2:for time, X_3:for temperature)

The constants in the equations were obtained from the following relationships (24).

for an amount of catalyst varied from 2.5 to 9 g.:

$$\frac{2.5-a}{b} = -1\ ,\ \frac{9-a}{b} = 1 \text{ and } a=5.75,\ b=3.25$$

for a time interval from 2 to 6 :

$$\frac{2-a}{b} = -1 \ , \ \frac{6-a}{b} = 1 \quad \text{and } a = 4 \ , b = 2$$

for a temperature range from 55 to 155 °C :

$$\frac{55-a}{b} = -1 \ , \ \frac{155-a}{b} = 1 \quad \text{and } a = 105, \ b = 50$$

A central composite design was built consisting of the experiments belonging to a 2^3 factorial design (experiments 1-8), six centre points (experiments 15-20) to analyse the lineer effect of each variable and six star points (experiments 9-14) to determine the quadratic effects with a value of $\alpha = 2^{3/4} = 1.682$.

Table 5 shows the correspondence between the natural and coded values of the three variables (catalyst amount, time and temperature) at different levels.

Table 5. Equivalance between the real and coded values of the variables analysed

variable	coded level -1.682	-1	0	1	1.682
catayst amount (g)	0.28	2.5	5.75	9	11.21
time (h)	0.63	2	4	6	7.36
temperature (°C)	21	55	105	155	189

The twenty design experiments and their yields of camphene (Y%) are shown in Table 6.

Table 6.Values of the experimental variables and camphene yield obtained

Exp. no	Variables			
	Cat. amount (g),for(X_1)	Time(h), for(X_2)	Temperature (C),for(X_3)	Respons Y(%)
1	2.5	2	55	0.42
2	9	2	55	0.42
3	2.5	6	55	0.97
4	9	6	55	0.88
5	2.5	2	155	42.84
6	9	2	155	34.86
7	2.5	6	155	39.74
8	9	6	155	34.83
9	0.28	4	105	0.61
10	11.21	4	105	13.42
11	5.75	0.63	105	1.16
12	5.75	7.36	105	10.31
13	5.75	4	21	0
14	5.75	4	189*	23.94
15	5.75	4	105	3.15
16	5.75	4	105	0.63
17	5.75	4	105	2.63
18	5.75	4	105	1.26
19	5.75	4	105	0.71
20	5.75	4	105	0.72

* This experiment was done at the department of Chemistry of Ege University in a high pressure reactor to obtain the reaction temperature of 189°C.

Consequently, the hypothesized model is:

$$Y=b_0+b_1X_1+b_2X_2+b_3X_3+b_{12}X_1X_2+b_{13}X_1X_3+b_{23}X_2X_3+$$

$$b_{11}X_1^2+b_{22}X_2^2+b_{33}X_3^2 \quad ....(24)$$

By using multiple linear regression techniques the regression coefficients were calculated. To calculate these coefficients lnY was used instead of percentage of yield. Resulted equation is:

$$\ln Y=0.209+0.571X_1+0.601X_2+1.818X_3-0.383X_1X_2-0.410X_1X_2$$

$$-0.588X_2X_3+0.267X_1^2+0.332X_2^2+0.456X_3^2 \quad \ldots(25)$$

To check the quality of fit a variance analysis was carried out by calculating the means of the sums of the squares corresponding to the different contributing sources to be considered: first order terms, second order terms, experimental error and lack of fit. Table 7 shows the analysis of the variance. Since the mean square for lack of fit is about the same size as the error mean square in Table 7, such an analysis appears to be adequate.

Table 7. Analysis of the variance

source	degrees of freedom	sum of squares	mean of squares	F_{cal}	F_{test}
1st order term	3	54.523	18.174	36.29	5.41*
2nd order term	6	10.037	1.673	3.34	4.95
lack of fit	5	9.921	1.984	3.96	5.05
error	5	2.504	0.501		
total	19	76.985			

When the calculated ratio between the square mean of each contribution and the square mean of the experimental error exceeds the tabulated F-test the effect of the analysed source of variation is considered significant (marked with an asterisk in Table 7) at the significance level of 95 % .

From Table 7; only first order terms are important, so equation 7 can be written simly:

$$\ln Y = 0.209 + 0.571X_1 + 0.601X_2 + 1.818X_3 \quad \ldots.(26)$$

The comparison of the experimental percentage yields of camphene with those obtained from Eq.26 is given in Table 8. From Table 8, it is clearly observed that at high temperatures,especially at 155°C, there is a great difference in the calculated and experimental yields.

Table 8. Calculated and experimental values of the camphene yield

catalyst amount (g)	time (h)	temperature (°C)	$Y_{exp.}$	$Y_{cal.}$
2.5	2	55	0.02	0.06
9	2	55	0.42	0.19
2.5	6	55	0.97	0.21
9	6	55	0.88	0.65
2.5	2	155	42.84	2.35
9	2	155	34.86	7.36
2.5	6	155	39.74	7.82
9	6	155	34.83	24.51
0.28	4	105	0.61	0.47
11.21	4	105	13.42	3.22
5.75	0.63	105	1.16	0.45
5.75	7.36	105	10.31	3.39
5.75	4	21	0	0.06
5.75	4	189	23.94	26.23
5.75	4	105	3.15	1.23
5.75	4	105	0.63	1.23
5.75	4	105	2.63	1.23
5.75	4	105	1.26	1.23
5.75	4	105	0.71	1.23
5.75	4	105	0.71	1.23

That is why, having the importance of linear terms of the model in mind, a new equation was developed for 155°C. For this purpose, additional experiments were carried out by varying the amount of catalyst and/or the reaction time, keeping the temperature constant at 155°C.The regression coefficients of the new equation were calculated by means of the least square techniques and the following equation with a regression coefficient of 0.34 was obtained:

$$Y = 38.97 - 0.699w + 0.665t \qquad ....(27)$$

w is the amount of catalyst(g), t is the reaction time (h).

Table 9 presents the comparison of the experimental and calculated values of the camphene yield at 155°C.

Table 9. Experimental and calculated values of the camphene yield at 155°C

Catalyst amount (g)	Time (h)	$Y_{exp.}$	$Y_{cal.}$
2.5	2	42.84	38.55
9	2	34.86	34.01
2.5	6	39.74	41.21
9	6	34.83	36.67
1	2	36.56	39.60
5	2	42.84	36.81
7.5	2	32.40	35.06
2.5	1	31.49	36.56
2.5	3	41.47	39.22
2.5	4	41.21	39.88
2.5	5	41.21	40.55

In order to visualize the obtained results better, the experimental and calculated yields were plotted against the amount of catalyst or the reaction time, as represented in Figures 5 and 6. As clearly understood from the regression coefficient and the figures, the agreement of the experimental data with the model applied is not satisfactory. That is why, several models such as exponential model have also been tried but it couldn't be possible to obtain a proper model to correlate the experimental data, probably, due to the high variety of the compounds (about 22 compounds, see Fig. 1 and Fig. 4) in the reaction studied.

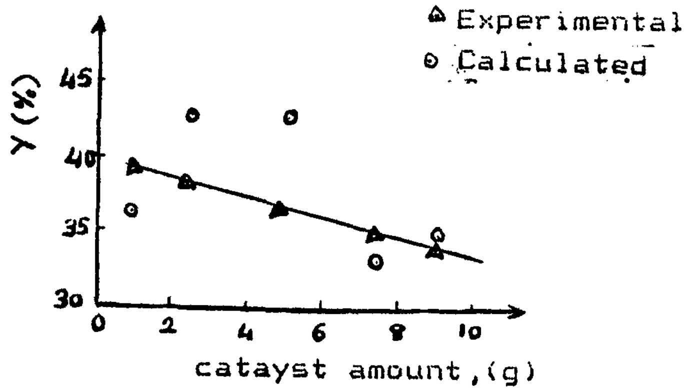


Fig.5 Calculated and experimental values of the yield of camphene with different catalyst amount for Zn at 155°C.

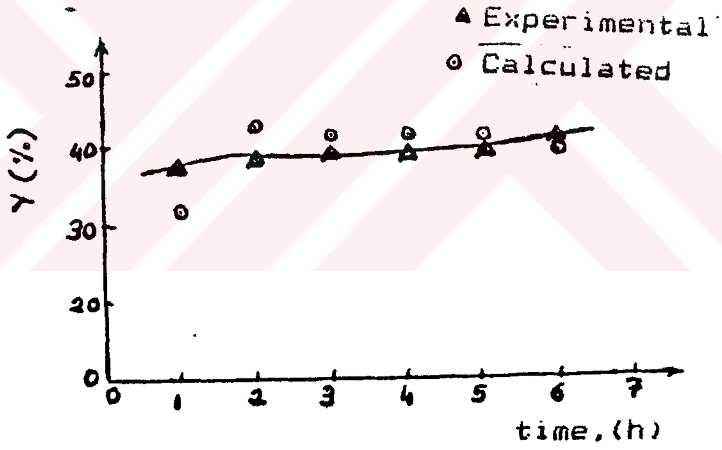


Fig.6 Calculated and experimental values of the campheneyield with time at 155°C,2.5g catalyst amount.

2.6. The Effect of Temperature on the Camphene Yield

To investigate the effect of temperature on the camphene yield, experiments were carried out at different temperatures keeping the amount of catalyst different temperatures keeping the amount of catalyst and the reaction time constant at 2.5g. and 2 hours (for the first set of runs) and at 5.75g. and 4 hours (for the second set of runs), respectively. The results are presented in Tables 10 and 11 and in Figures 7 and 8.

Table 10. Effect of temperature on the camphene yield at 2.5 g. and 2 hrs.

Temperature (°C)	% Camphene Yield
55	0.02
120	0.55
130	4.25
140	13.60
155	42.84

Table 11. Effect of temperature on the camphene yield at 5.75 g. and 4 hrs.

Temperature (°C)	% Camphene Yield
21	0
105	1.52
189	23.94

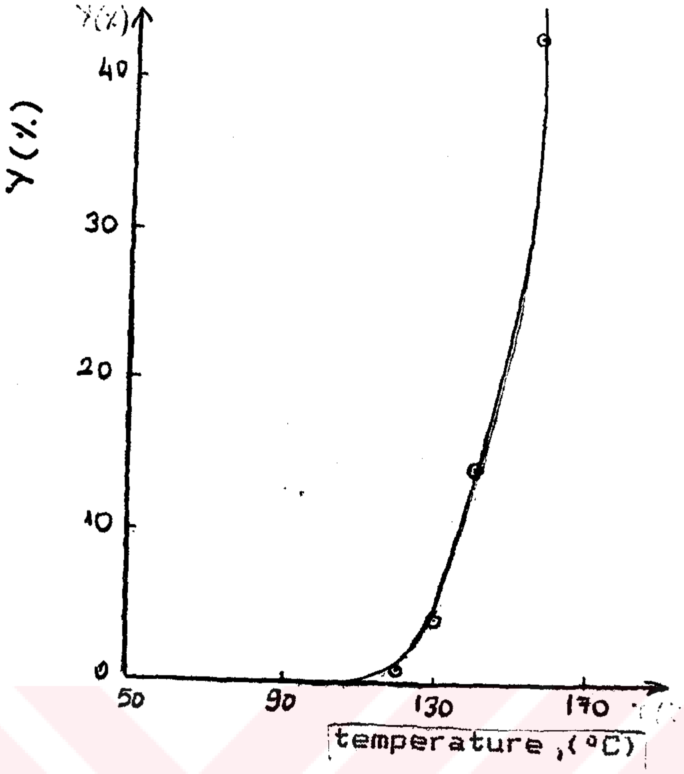


Fig.7. Variation of the yield of camphene with temperature at 2.5 g. for 2 hrs.

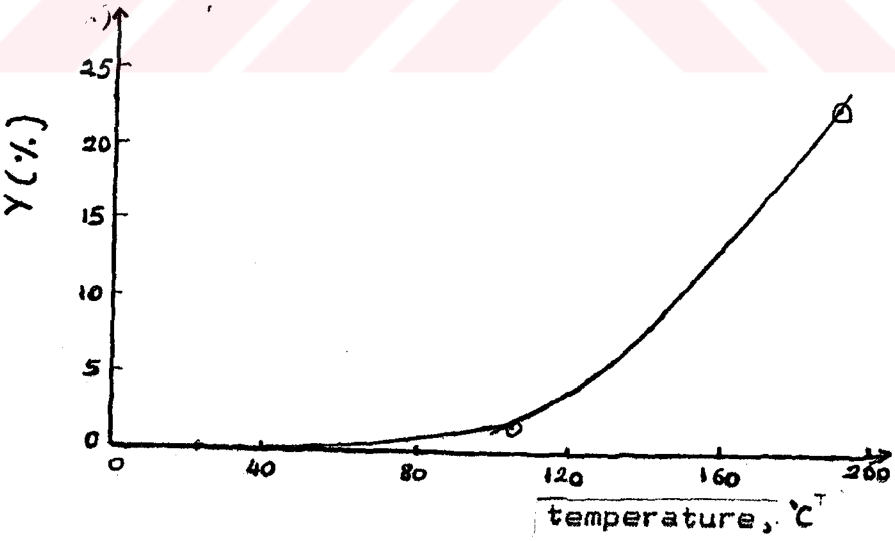


Fig.8. Variation of the yield of camphene with temperature at 5.75 g. for 4 hrs.

Figure 7 shows the relation between temperature and yield of camphene at 2.5 g. for 2 hrs. Below 130°C yield of camphene is almost zero. After 140°C, yield of camphene suddenly increases and maximum yield is obtained at 155°C. Figure 8 gives the temperature dependency of yield for a catalyst amount of 5.75 g. for a reaction time of 4 hours.Similar to the trend in Fig.7, as the temperature increases the yield of camphene also increases. But this increase is not as drastic as in Fig.7 . The yield obtained at 189°C is rather smaller than that at 155°C although the amount of catalyst used is two times greater than that in Fig.7 .

2.7. The Effect of Catalyst Amount on the Camphene Yield

The effect of catalyst amount was investigated at 155°C for 2 hours and at 105°C for 4 hours, respectively by varying the amount of catalyst. The results of these experiments are shown in Tables 12 and 13 and Figures 9 and 10, respectively.

Table 12. Effect of catalyst amount on the camphene yield at 155°C for 2hrs.

Catalyst amount (g)	% Camphene Yield
1	36.56
2.5	42.84
5	42.84
7.5	32.40
9	34.86

Table 13. Effect of catalyst amount on the camphne yield at 105°C for 4 hrs.

Catalyst amount (g)	% Camphene Yield
0.28	0.61
5.75	1.52
11.21	13.42

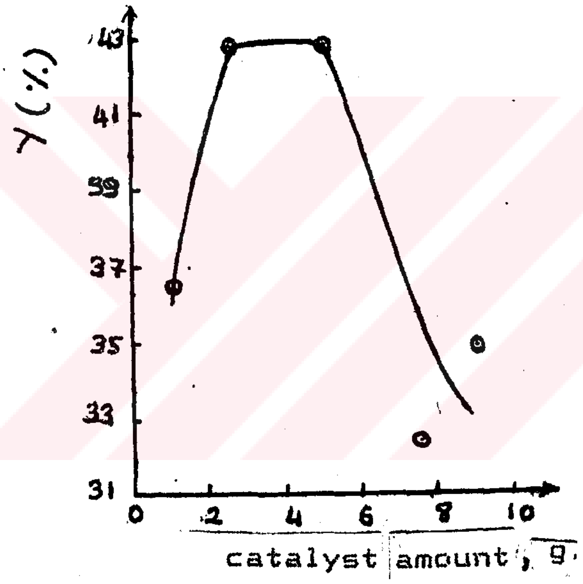


Fig. 9. Variation of the yield of camphene with catalyst amount at 155°C for 2 hrs.

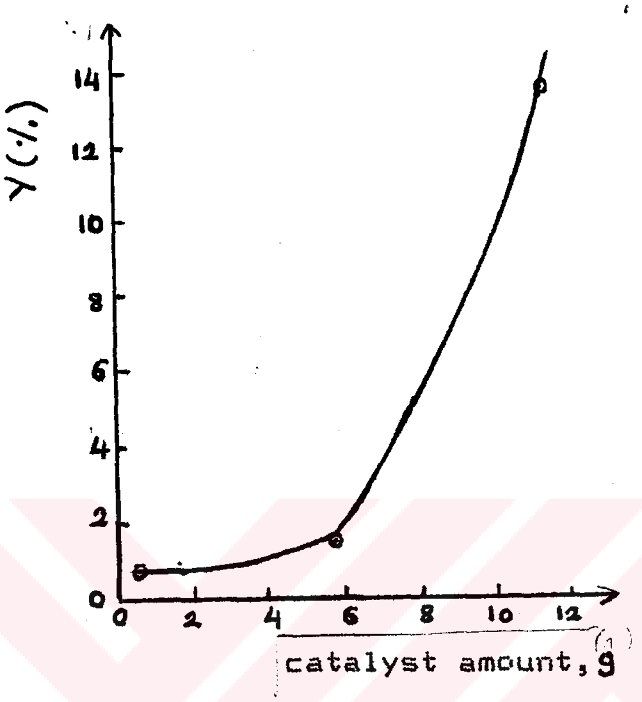


Fig.10. Variation of the yield of camphene with catalyst amount at 105°C for 4 hrs.

Figure 9 indicates that the yield of camphene increases with increasing catalyst amount until a catalyst amount 2.5 g. is reached, between 2.5 g. and 5 g., yield remains constant and then yield begins to decrease with increasing catalyst loading. From Figure 9, it is clearly seen that the optimum catalyst amount at 155°C is 2.5 g. and the maximum conversion obtained is 42.84 % . The decrease in camphene yield after 5 g. catalyst may arise from the inhibition effect of products produced on the formation rate of camphene.

As shown in Fig. 10 at a reaction time of 4 hours and for a reaction temperature of 105°C, the yield of camphene increases as the catalyst amount increases, as observed in the case at 155°C. But the yield of camphene is very low due to the low reaction temperature even though higher amount of catalyst and longer reaction time than those in Fig. 9 are used.

2.8. The Effect of Reaction Time on the Camphene Yield

The effect of time on the camphene yield was studied by varying the reaction time at 155°C and at a catalyst amount 2.5 g. and also at 105°C keeping the catalyst amount constant at 5.75 g., respectively. The results of the experiments for two cases are displayed in Tables 14 and 15 and Figures 11 and 12.

Table 14. Effect of time on the camphene yield at 155°C and 2.5 g.

Time (h)	% Camphene Yield
1	31.49
2	42.84
3	41.47
4	41.21
5	41.21
6	39.74

Table 15. Effect of time on the camphene yield at 105°C and 5.75 g.

Time (h)	% Camphene Yield
0.63	1.16
1.52	1.52
10.31	10.31

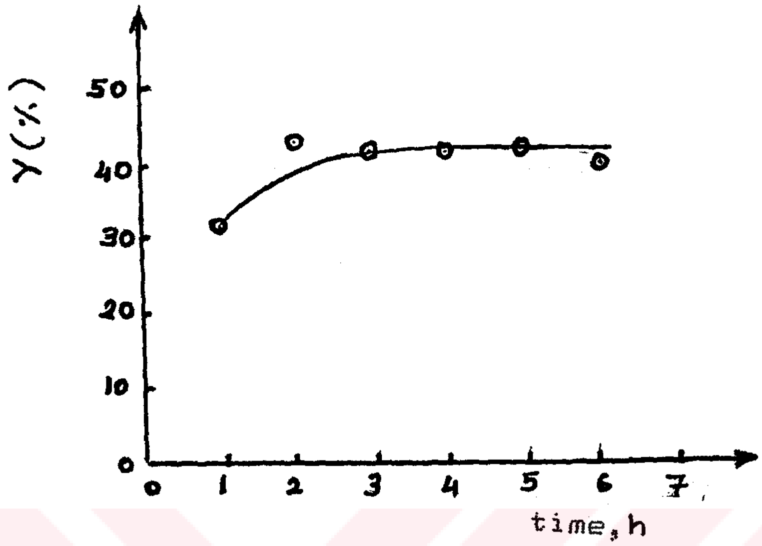


Fig. 11. Variation of the yield of camphene with time at 155°C and 2.5 g.

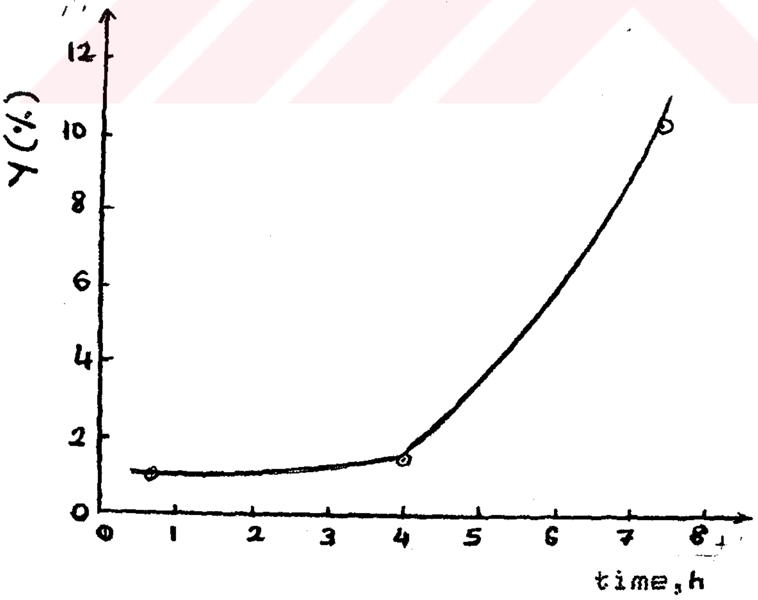


Fig. 12. Variation of the yield of camphene with time at 105°C and 5.75 g.

Figure 11 indicates that the yield of camphene doesn't change with time, it remains almost constant at 155°C. The relation between the yield of camphene and time at 105°C and at catalyst amount of 5.75 g. is shown in Figure 12. According to this figure, yield increases with time. But the yield, even at a longer reaction time (7.36) with a more than twice amount of the catalyst in Fig.12, 5.75 g., is fairly low than the yield at 155°C and at a catalyst amount of 2.5 g. due to the low reaction temperature.

2.9. The Effect of Stirring Speed on the Camphene Yield

As known, in liquid phase heterogeneous catalytic reactions, the reaction mixture is stirred vigorously slurrying the catalyst uniform by throughout the liquid. In the present study such a good mixing was obtained keeping the stirrer switch at 5 constant. Hence, the stirring speed was kept constant at that value in all the experiments studied. But in order to observe the effect of stirring speed on camphene yield, some experiments were carried out at different stirring speeds keeping the other parameters constant. The results are shown in Table 16. There is no an important difference between the camphene yields obtained at different stirring speeds although a slight increase in yield with increasing stirring speed is observed. These results show that the reaction mixture is well mixed and there is no catalyst particle remaining at the bottom due to gravity.

Table 16. Effect of stirring rate on the camphene yield at 155°C and 2.5 g. for 2 hrs.

Position of stirrer switch	% Camphene Yield
3	41.93
5	42.84
7	43.1

2.10. The Effect of Catalyst Particle Size on the Camphene Yield

It is well known that in heterogeneous catalytic reactions, the decrease in particle size increases the rate of reaction, decreasing the internal diffusion resistances (high effectiveness factor). In literature, for the isomerization of α-pinene to camphene, it is noted that although reaction rates increase with increase in the fineness of the catalyst, little effect of fineness is observed above grain size of about 0.075 mm. That is why, catalyst particles with a size of between 0.075-0.1 mm. were used in all the experiments except the runs mentioned below. To investigate the effect of particle size on camphene yield, experiments were done at different catalyst particle sizes, keeping the other parameters constant. Table 17 shows the results.

From the Table 17, it is understood that at a particle size greater than 1 mm., the camphene yield is rather smaller than that with a size of 0.075 mm.The decrease in size from 0.075 mm. to 0.040 mm. causes a small decrease in yield from 42.84 to 37.86 .Such a negative effect of size may be probably observed due to the some errors made during the runs.

Table 17. Effect of particle size on the camphene yield at 155°C and 2.5 g. for 2 hours

Particle Size (mm)	% Camphene Yield
$d_p < 0.040$	37.86
$0.075 \leq d_p \leq 0.01$	42.84
$1 \leq d_p \leq 2$	16.37

2.11. The Effect of the Type of Catalyst Addition to the Reaction Mixture

In one experiment at 155°C at 2.5 g. catalyst, at a reaction time of 2 hours, half of the catalyst amount was charged to the flask at the beginning of the run and the remaining part of the catalyst was added to the mixture after 1 hour. The yield of camphene was found to be 34.42 % The run was repeated at the same conditions but by adding all of the catalyst to the mixture at the beginning of the experiment, the yield of camphene was 42.84 % . So, it is concluded that there is a negative effect of the addition of catalyst in two steps on the yield.

2.12. Kinetics of the Isomerization Reaction of α-Pinene

From the GC analysis of the products in the isomerization reaction of α-pinene, it is seen that the main products are camphene and limonene (see Fig. 4). Hence, the reaction may be considered as a parellel reaction system given below, neglecting the formation of other by-products in rather low conversions.

$$\begin{tikzcd}
\alpha\text{-pinene} \arrow[r] \arrow[dr] & \text{camphene} \\
& \text{limonene}
\end{tikzcd}$$

To investigate the order such a reaction system, experiments were done at different temperatures between

130 and 155°C keeping the reaction time at 2 hours and catalyst amount at 2.5 g. constant. The samples withdrawn periodically were analysed after the seperation of catalyst from the liquid phase by centrifucal forcing.

Table 18 - 20 and Figures 14 - 16 present the variations of several conversions with time at different temperatures where the total conversion of α-pinene is X_t, the conversion of α-pinene to camphene (or yield of camphene, that is, the fraction of α-pinene converted to camphene) is X_c and the conversion to limonene is X_l. As seen, conversions to the products, that is X_t, X_c and X_l, increase with increasing reaction time. As the temperature increases conversion to products also increases which supports the parellel reaction system.

Table 18 .Variation of conversions and selectivity at 130°C

t(min)	X_c	X_l	X_t	S_o
20	0.02	0.34	1.81	0.05
40	0.91	0.97	2.42	0.93
60	1.94	1.44	5.08	1.35
80	2.28	1.95	5.54	1.17
100	3.12	2.53	7.22	1.23
120	4.25	3.32	9.47	1.28

Table 19. Variation of conversions and selectivity at 140°C

t(min)	X_c	X_l	X_t	S_o
20	0.85	0.92	1.43	0.92
40	1.29	1.23	1.55	1.05
40	2.99	2.39	5.44	1.25
60	4.13	3.04	7.83	1.36
60	5.59	4.20	10.25	1.33
80	6.80	5.06	13.56	1.34
80	8.55	6.14	17.42	1.39
100	9.55	6.88	18.74	1.39
120	13.60	9.37	25.59	1.45

Table 20. Variation of conversions and selectivity at 155°C

t(min)	X_c	X_l	X_t	S_o
20	11.42	8.34	25.51	1.37
40	20.53	14.46	44.62	1.42
60	31.39	20.31	68.68	1.55
,80	32.34	21.73	71.78	1.49
100	40.94	25.29	88.21	1.62
120	42.55	25.56	92.75	1.66

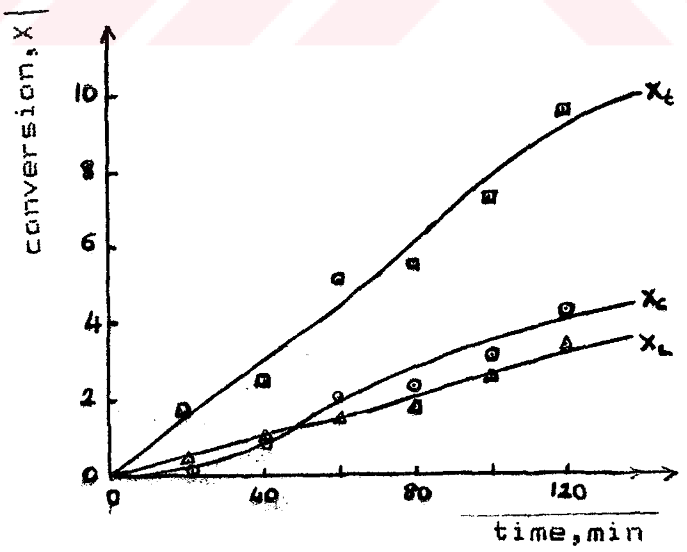


Fig. 14 Variation of the conversion of α-pinene, camphene and limonene at 130°C.

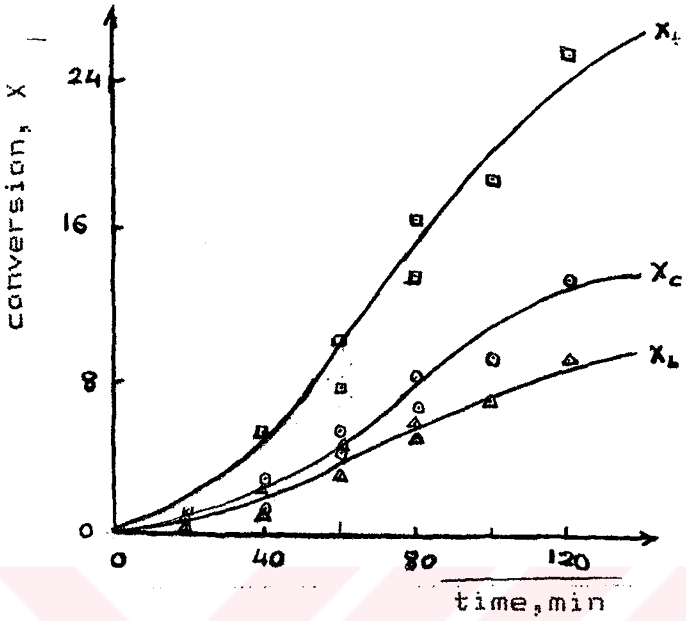


Fig.15. Variation of the conversions of α-pinene, camphene and limonene at 140°C

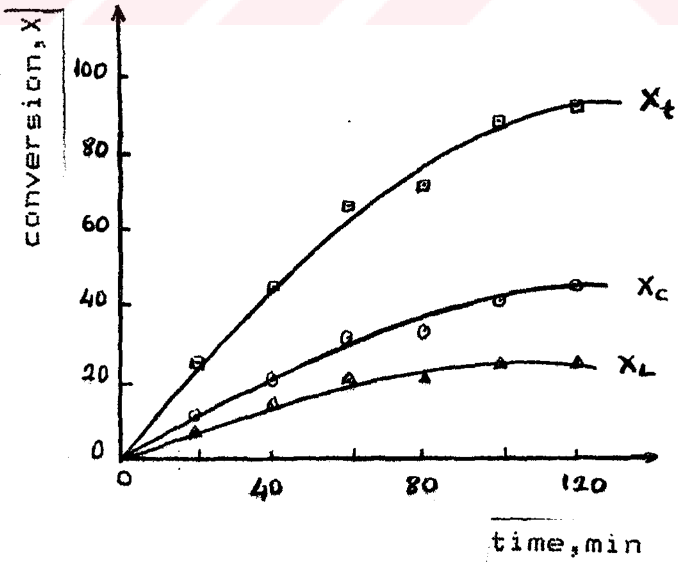


Fig.16 Variation of the conversions of α-pinene, camphene and limonene at 155°C

The overall selectivity of camphene, S_c, is the ratio of the yields of camphene and limonene. Because the amount of a product produced is proportional to the yield, $S_c = X_c / X_l$ can be written. The selectivity of campnene, S_c, obtained at different temperatures are given in Figures 17-19 as a function of time. It is clear from these figures that selectivity increases with time and with temperature. The selectivity is the highest at 155°C approaching to 1.7 .

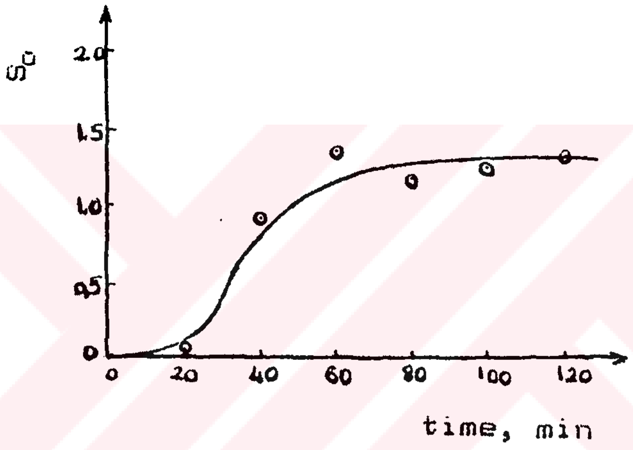


Fig. 17. Selectivity of camphene at 130°C

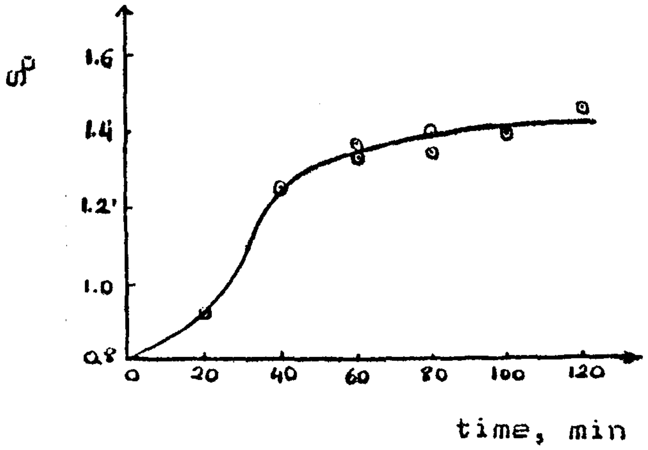


Fig.18. Selectivity of camphene at 140°C

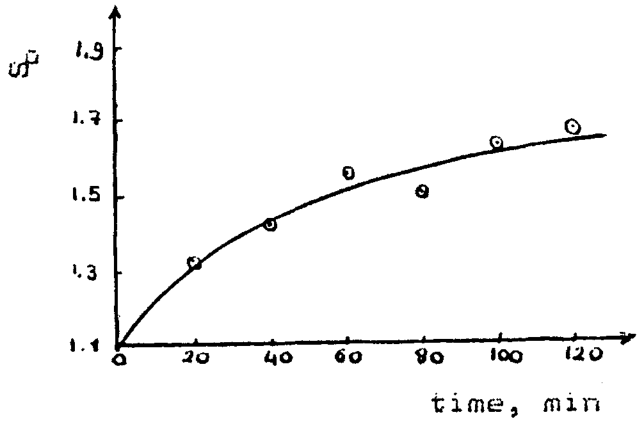


Fig.19. Selectivity of camphene at 155°C

If the isomerization of α-pinene is considered as a first order parellel reaction system, the rate of disappearence of α-pinene and the rates of formation of products, camphene and limonene can be given by equations 11-13.

According to Equation 14, plotting experimental values of $-\ln(C_A/C_{Ao})$ versus time (t), $(k_1+k_2)\frac{V_1}{M_C}$ is obtained from the slope of the straight line. Figures 20-22 show these plots at different temperatures. From the figures, it is seen that the disappearance rate of α-pinene may be considered as a first order reaction.

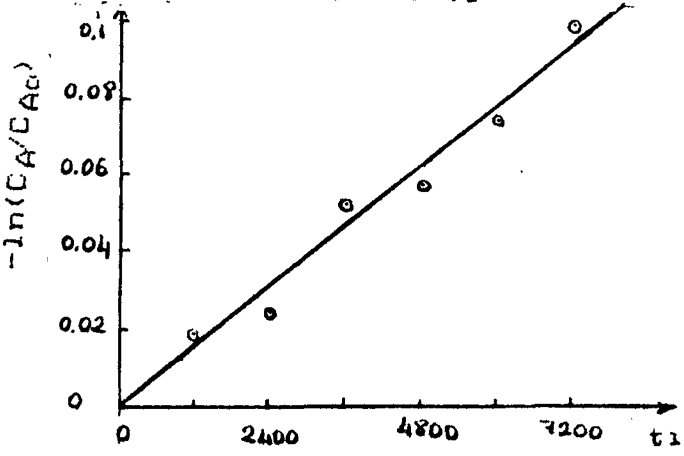


Fig.20. Variation of $-\ln(C_A/C_{Ao})$ with time at 130°C

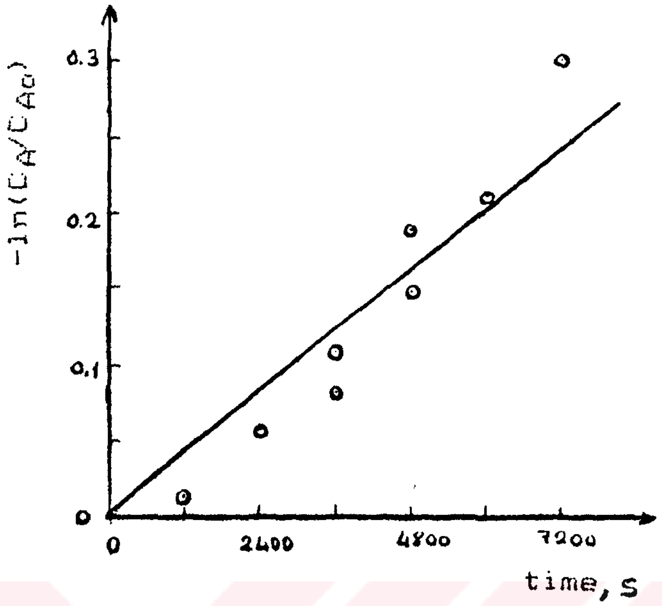


Fig.21. Variation of $-\ln(C_A/C_{Ao})$ with time at 140°C

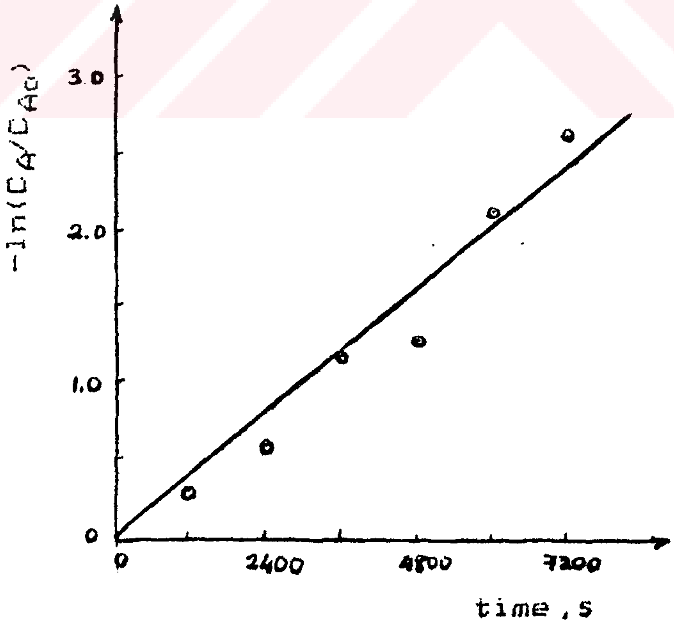


Fig.22. Variation of $-\ln(C_A/C_{Ao})$ with time at 155°C

If in Equation 19 , the conversion of camphene is plotted versus the conversion of limonene, a straight line would be obtained with a slope being k_1/k_2. Figure 23-25 show these plots at different temperatures. From k_1+k_2 and k_1/k_2 values calculated at different temperatures, k_1 and k_2 can be determined separately.

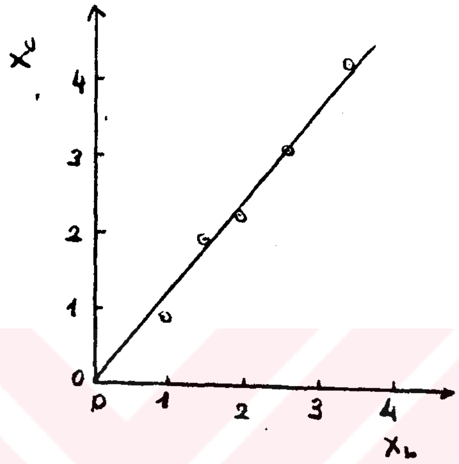


Fig.23. Variation of X_c with X_l at 130°C

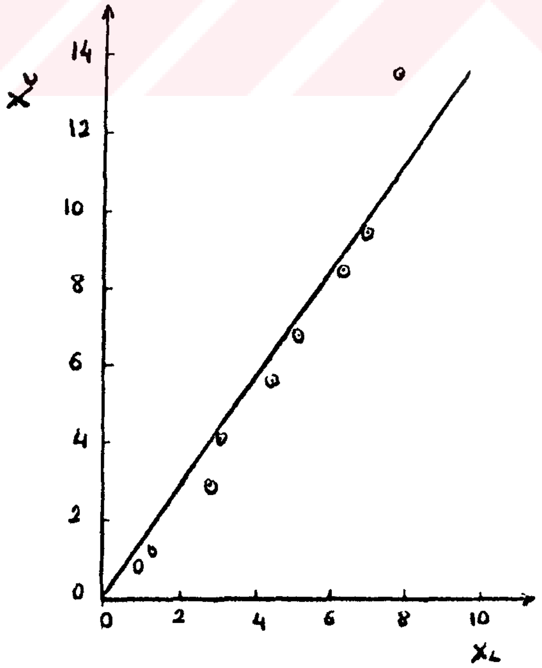


Fig.24. Variation of X_c with X_l at 140°C

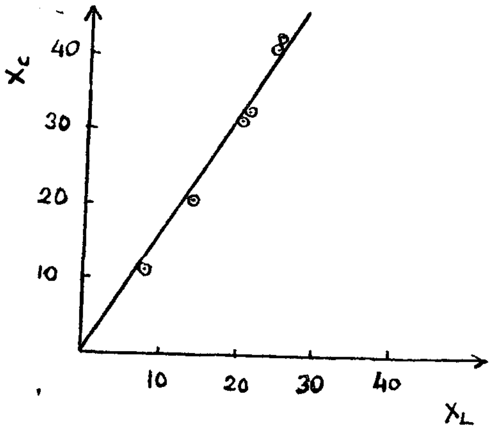


Fig.25. Variation of X_c with X_1 at 155°C

Table 21 presents the rate constants k_1 and k_2 calculated for temperatures 130°C, 140°C, 155°C.

Table 21. Rate constants for different temperatures

Temperature (°C)	k_1 (l/g.sec)	k_2 (l/g.sec)
130	2.082×10^{-4}	1.683×10^{-4}
140	5.663×10^{-4}	4.060×10^{-4}
155	6.002×10^{-3}	3.823×10^{-3}

To investigate the dependency of the rate constant on temperature logarithmic form of Arrhenius equation is used. Figures 26 and 27 show the Arrhenius plots for the production of camphene and production of limonene.

From the slopes and intercepts of the straight lines in Figures 25-26 activation energies and frequency factors of k_1 and of k_2 are calculated. Between 130 and 155°C, for the production of camphene:

$$k_1 = 3.020\times10^{-2}e^{-33381.60/RT}$$

and for the production of limonene:

$$k_2 = 1.576x10^{-2}e^{-31096.53/RT}$$, where R in cal/gmol K

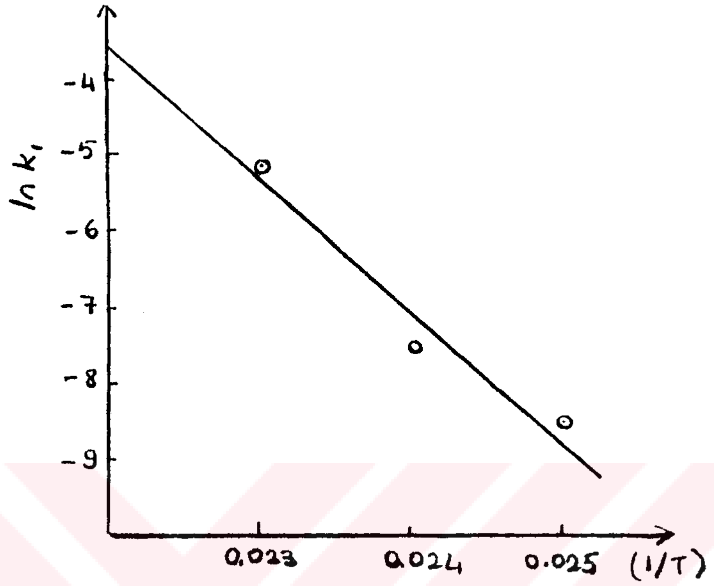


Fig. 26 Plot of Arrhenius Equation for the production of camphene

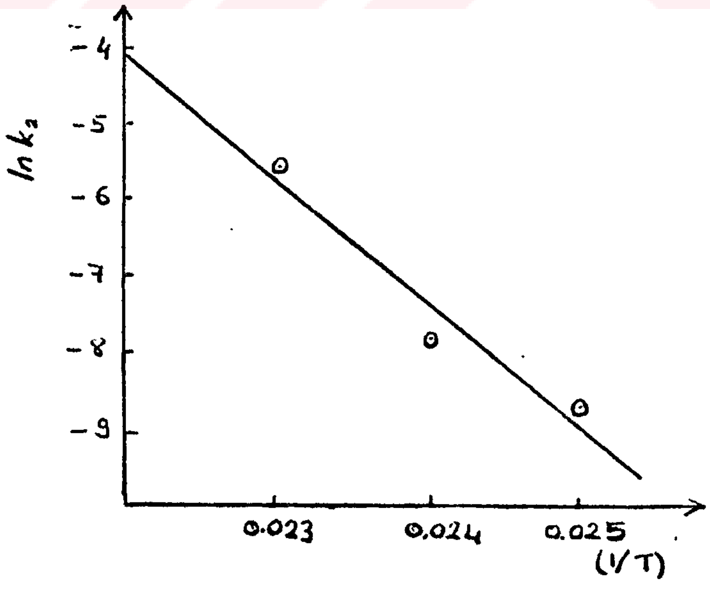


Fig.27 Plot of Arrhenius Equation for the production of limonene

The reaction mixture is stirred vigorously slurrying to catalyst uniform throughout the liquid during the runs. The turbulence created around the catalyst particle helps to eliminate the external diffusion resistance between the bulk liquid and the surface of the catalyst. Internal diffusion resistances are also negligible due to the very small size of catalyst particles used in the runs ($0.075 \leqslant d_p \leqslant 0.1$mm).

As seen from Figures 26 and 27 a rather good straight lines are obtained on the Arrhenius plots, showing that the external diffusion resistances are negligible and the activation energies calculated are true activation energies.

The point selectivity of camphene with respect to limonene, S_p, is the ratio of the rate constants as given in Eq. 7.

Table 22 presents the point selectivities at different temperatures.

Table 22. Point selectivity of camphene with respect to limonene

Temperature (°C)	$S_p=k_1/k_2$
130	1.24
140	1.39
155	1.57

As seen from Table 22, point selectivity increases with increasing temperature. As known, point and overall selectivities are identical for first order parellel reaction systems (18). The comparison of point selectivity (Table 22) with the overall selectivity of camphene (Table 18-20) shows that both the selectivities are equal to each other, supporting that the isomerization reaction of α-pinene can be considered as a first order parellel reaction system.

3. Results and Discussion

In this work, heterogeneous catalytic isomerization reaction of α-pinene to camphene has been investigated. Eleven different catalysts were prepared employing halloysite, activated clay, titanium dioxide, activated carbon and clinoptilolite which was a natural zeolite and selectivity to camphene was determined at 155°C. The most selective catalyst was found to be the natural zeolite composed of 74.86 % SiO_2, 0.42 % Fe_2O_3 , 0.70 % MgO , 0.50 % Na_2O , 2.71 % K_2O , 9.04 % H_2O , 2.42 % CaO , 9.35 % Al_2O_3 . Although the catalyst of activated clay 2 seemed to be the most selective one from the point of the amount of catalyst used in a run, it wasn't selected because acid clay catalyzed isomerization reactions of α-pinene were rather uncontrollable, leading to severe explosions as reported in literature and oserved in the present work. A central composite rotatable design was used to obtain a relationship between the yield of camphene and catalyst amount, time and temperature. But it could not be possible to find a proper model satisfying the experimental data.

Camphene yield was increased by increasing reaction temperature, the maximum yield was obtained at 155°C as 42.84 % in the temperature range studied. The increase of temperature from 155°C to 189°C caused a drastic decrease in camphene yield even at high catalyst amounts and at longer reaction times. Such a result was also reported by Popov and Vyrodov (13) in literature. Increasing catalyst amount from 2.5 g. to 5 g. ,didn't change the yield of camphene at 155°C but above 5 g. of catalyst a decrease in camphene yield was observed. At lower temperatures than 155°C, yield increased with catalyst amount. The reaction time was not dominant on the camphene yield after two hours at

155°C although there is a slight increase in yield during the change of reaction time from one hour to two hours. At low temperatures, yield was increased by time. A negligible effect of stirring speed on the camphene yield was observed in the range studied. As known, in heterogeneous catalytic reactions, the decrease in particle size increases the rate of reaction, decreasing the internal diffusion resistances (18). Our results also obey this rule. Yield of camphene decreased with increasing particle size.

From the experimental results, the optimum conditions for the isomerization of α-pinene were found as follows: (for 100 g. of wood turpentine containing 85 % in weight α-pinene)

Reaction temperature : 155°C
Amount of catalyst : 2.5 g.
Reaction time : 2 hours
Catalyst particle size : $0.075 \leq d_p \leq 0.1$ mm.

The isomerization reaction of α-pinene to camphene can be considered as a parellel reaction system with main products of camphene and limonene, neglecting the formation of side products in low conversions. Such a model fitted the experimental data fairly well. From Arrhenius plots of the rate constants between 130-155°C, for the production rate of camphene :

$$k_1 = 3.020 \times 10^{-2} e^{-33381.6/RT}$$

for the production of limonene :

$$k_2 = 1.576 \times 10^{-2} e^{-31096.53/RT}$$

were obtained. As seen, activation energy for the production of camphene is greater than that for the production of limonene. From the general rule on the influence of temperature on the relative rates of competing reactions saying that a high temperature favors the reaction of higher activation energy, a low temperature favors the reaction of lower activation energy (25), high tamperature should be used to promote the production rate of camphene. Experimental results also support this rule . Selectivity to camphene increases with temperature and the highest selectivity is obtained at 155°C.

It is reported in literature that under proper conditions of pressure, temperatures up to 200°C or higher may be used to obtain a more favorable product distribution. That is why, in future isomerization α-pinene may be investigated at high pressures.

4. SUMMARY

In this study, the catalytic isomerization of α-pinene to camphene was investigated. The most selective catalyst and operating conditions were examined and kinetics of the reaction was also investigated.

The most selective catalyst was found to be clinoptilolite (natural zeolite) with a composition of 74.86 % SiO_2, 0.42 % Fe_2O_3, 0.70 % MgO, 0.50 % Na_2O, 2.71 % K_2O, 9.04 % H_2O, 2.42 % CaO, 9.35 % Al_2O_3. Optimum production conditions of camphene by the isomerization reaction of α-pinene were as follows: reaction temperature 155°C, reaction time 2 hours and catalyst amount 2.5 g. At these optimum conditions the yield of camphene was 42.84 % .

The kinetic investigation of the isomerization reaction of α-pinene showed that reaction is a first order parellel system. Main products of the reaction were camphene and limonene. Rate constants for the production of camphene and for the production of limonene were obtained as $k_1 = 3.020 \times 10^{-2} e^{-33381.6/RT}$ and $k_2 = 1.576 \times 10^{-2} e^{-31096.53/RT}$, respectively , at the temperature range 130 - 155°C.

5. REFERENCES

1.Othmer, K., ;Encylopedia of Chemical Technology,Third Edition, Volume 22, USA., John Wiley and Sons, 1983.

2.Carson, W.F.; Prepation of Camphene from α-Pinene, US Patent 2 382 397, 1945

3.Kirkpatrick, W.J.; Isomerization of Pinene to Camphene,US Patent 2 385 711, 1945

4.Vedenev, K.P., Bordyshev,I.I.; Use of Gas-Liquid Chromotography to Control the Isomerization of α-Pinene to Camphene, Lesokhim. Prom., 21(1), 15-16,1968

5.Korotov, S.V., Vyrodov, V.A., Afanas'eva, E.V., Kolesov, A.I., Maslakova, Z.L., Oblivantseva, T.D., Chirkov, P.K., Zhurovlev, P.I., Minaeva, O.I.; Camphene, USSR Patent 238-541,1969

6.Petelina, L.P., Dzhondosova, K.D., Goryaev, M.I.;Substances present in essential oils. Effect of the Exchange capacity and swelling ability of the sulfonated cation exchange resin Ankalite KT-3 on the Isomerization of α-pinene to Camphene, Izv.Akad.Nauk Kaz.SS.R, Ser. Khim.,19(2),53-57,1969

7.Afanas'eva, E.V.,Vyrodov, V.A.,Korotov, S.V.;Continuous Isomerization of pinene into Camphene, 2.Isomerization of Pinene into Camphene in a three Phase system, Nauch. Tr.,Leningrad, Lesotekh. Akad.,135(1), 11-19, 1970

8.Afanas'eva, E.V., Vyrodov, V.A., Korotov, S.;Continuous Isomerization of Pinene into Camphene, 3.Isomerization of Pinene into Camphene in a three Phase system on an Experimental Industrial Apparatus, Nauch. Tr., Leningrad, Lesotekh. Akad., 135(1), 20-25, 1970

9.Matsubara, Y.,Butani, Y., Wakabayashi, S., Watanabe, Y., Takamatsu, A., Morita, M.;Camphene, Japon Patent 7028575, 1970

10.Davis, C.B., McBride,J.J.; Catalytic Isomerization of Alpha-Pinene, US Patent 3842 135, 1974

11.Nazir, M., Ahmad, M., Chaudhary, F.M.;Isomerization of α-Pinene to Camphene using indigenous Clays as Catalysts, Pak.J.Sci.Ind.Res., 19(3-4), 175-178, 1976

12.Bardyshev, I.I., Manukov,E.N., Chuiko,V.A.;Chemical Reactions of Pinenes in the presence of Salicylic acid, Vestsi Akad .Navuk BSSR, Ser.Khim.Navik, 6 ,87-94, 1977

13.Popov, A. A., Vyrodov, V. A. ; Isomerization Transformations of Pinene in the presence of Activated Titanium Oxide, Gidroliz, Lesokhim Prom-St, 6, 18-20, 1979

14.Kullaj,S.;Albanian Clays as Catalysts in the Isomerization of α-Pinene into Camphene and Tricyclene, Bull.Shkoncave Nat.,39(4), 47-55, 1985

15.Kullaj,S.;Effect of the Characteristic of Activated Clays on their ability to lead to isomerization of α-pinene into camphene and tricyclene, Bull. Shkoncave Nat., 43(1), 81-85, 1989

16.Battolova, S.B., Mukitanova, T.R., Tabenova, K.G.;Dependence of the Selectlvity of an Industrial Titanium Catalyst for α-pinene Isomerization on the Content of exchanged sodium ions, Vestn. Akad. Nauk. Kaz. SSR., 10, 52-56, 1990

17.Ozek, T.;Production of Odorous Compounds from the Natural Monoterpenes, Ph.D. Thesis, Anadolu University, Medicinal Plants Research Centre, Eskisehir, 1994

18.Smith, J.M.;Chemical Engineering Kinetics, Third Edition, USA, McGraw Hill, 1981

19.Yolgormez, S.;Activated Carbon (from Nut Shell), Diploma project, Ege University, Chem. Eng. Dep., 1991

20.Besun N.;Bentonit turu killerden aktif toprak eldesinde optimum parametrelerin saptanmasi ve pilot tesis tasarimi,Ph.D.Thesis, Ege university, Chem. Eng. Dep.,1990

21.Arata,K., Tanabe, K.; Isomerization of α-pinene oxide over over Solid Acids and Basis, Chemistry , Letters, 1017-1018, 1979

22.Lipson, C., Sheth, N.J.; Statistical Design and Analysis of Engineering Experiments, USA, McGraw Hill, 1973

23.Gonzolez-Velasco, J.R., Gutierrez-Ortiz, M.A., Gutierrez-Ortiz, J.I., Gonzelez-Marcos, M.P., Gonzelez-Marcos, V.A.; Techno-economic Optimization of Isomerization of Maleic Acid to Fumaric Acid Using Ammonium Bromide as a soluble Catalyst, Chem. Eng. Process, 30, 15-21, 1991

24.Cochran, W.G., Cox, G.M.; Experimental Designs, Second Edition, USA, John Wiley and Sons, 1957

25.Levenspiel, O.;Chemical Reaction Engineering, Second Edition, USA, John Wiley and Sons, 1972