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MODIFIED ZEOLITE CATALYST FOR SELECTIVE DIALKYLATION OF NAPHTHALENE

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Abstract

The dialkylation of naphthalene with isopropanol to produce 2,6-diisopropylnaphthalene (2,6-DIPN) was carried out over HY zeolite. The effects of various reaction conditions, such as pressure, temperature, space velocity, molar ratio of alcohol to naphthalene and time on stream (TOS) on product distribution were studied. HY zeolite was modified by transition metals, such as Fe³⁺, Ni²⁺, Co²⁺ and Cu²⁺ using wet impregnation method to maximize the selectivity to 2,6-DIPN. The catalysts were characterized by XRF, XRD, TGA, nitrogen adsorption-desorption and Temperature Programmed Desorption of t-Butylamine. Under optimum reaction conditions, (50 bar, 220 °C, isopropanol/naphthalene = 4 (mole ratio), WHSV = 18.8 h⁻¹, TOS 6 hours), HY zeolite modified by Fe³⁺ was found to give the highest selectivity, by increasing the 2,6/2,7-DIPN ratio from 2.8 to 6.6. The experimental results indicate that the selectivity to 2,6-DIPN is in the order of Fe-HY>Ni-HY>Cu-HY>Co-HY>HY. Naphthalene conversion of 77% was obtained over HY zeolite, while after modification by Fe, Co, Ni and Cu, the conversion was changed to 73, 76, 88 and 96%, respectively. TGA analysis of used catalyst samples revealed that a higher amount of PIPN was produced on zeolite modified by Co and Cu. This confirms that PIPN molecules are possible coke precursors, and therefore led to larger amount of coking on the Co-HY and Cu-HY catalysts.

Keywords

Dialkylation, isopropylation, naphthalene, HY zeolite, wet impregnation

1. Introduction

Dialkylated naphthalenes, such as 2,6-diisopropyl naphthalene (2,6-DIPN) are of great commercial interest. 2,6-DIPN can be oxidised to 2,6-naphthalene dicarboxylic acid, which is used as a monomer to manufacture polyethylenenaphthalate (PEN) polymers and copolymers with superior properties [1]. The key to the large-volume application of these materials (as fibres, films, resins, and engineering plastics) is to develop highly efficient catalytic process for the desired monomers, in particular 2,6-dialkylated naphthalene (2,6-DAN). The use of shape selective zeolites in the alkylation of naphthalene has advantages such as low cost, re-usability and lower impact on the environment compared with conventional homogeneous Friedel-Craft reactions.

The acidic nature of zeolites, their high activity and unusual selectivity, make them suitable for many acid catalyzed reactions [2-4]. Various zeolite catalysts, such as HY, H β , HZSM-5, Mordenite, SAPO-5 and MCM-41 have been studied extensively for the alkylation of naphthalene and proved to be the most promising solid acidic catalysts for highly selective production of 2,6-DAN [5-7]. The formation of 2,6-DAN with a 2,6/2,7 ratio of 2 to 3 was observed over HY and H β zeolites, while higher selectivity over H-Mordenite of around 5.7 ratio was reported by Maheswari and coworkers [8]. H-Mordenite exhibits very high shape selectivity, but suffers from low activity owing to its narrow pores. It is therefore challenging to achieve both high activity and high 2,6-DAN selectivity. Many efforts have been made to improve the shape selectivity of zeolites by modification of their acidity, porosity and stability. Introduction of guest elements as cations inside the zeolite structure decreases its total surface area but can increase its number of acidic centers. The effects of ion exchanged zeolite with alkali, alkaline earth, transition metals and rare earth cations on many different Friedel-Crafts reactions have been studied but there are a lack of data on performance of these catalysts for selectivity and activity of zeolites for alkylation of naphthalene [9-11]. Kamalakar et al. [12] reported ethylation of naphthalene over HY and HMCM-41 zeolite modified by La³⁺, Ce³⁺ and

1 Mg²⁺ cations. They concluded that CeMgY (5 wt. % Ce, 3 wt. % Mg) is a good catalyst with 57.2%
2 conversion and 31.3% selectivity to 2,6-DAN after 4 hours. This was attributed to Ce³⁺ increasing the
3 alkylation activity and thermal stability of catalyst, whilst Mg²⁺ optimises the acidity to decrease coke
4 formation. In similar work, Kamalakar and coworkers [13] modified HY, HMCM-41 and SAPO-5
5 zeolite with Ce³⁺, Fe³⁺ and potassium cations and reported that modification of HY zeolite with Ce³⁺,
6 Fe³⁺ increased the selectivity to 2,6-DAN from 9.8% for parent HY to 25.2% and 20.4% for CeKY
7 and FeY, respectively after 4 hours. Apart from research by Kamalakar's group, little work has been
8 done to investigate the performance of zeolite modified by transition metals in the alkylation of
9 naphthalene. In light of this, in the current paper the effects of reaction conditions (temperature,
10 pressure, weight hourly space velocity, isopropanol/naphthalene molar ratio) on naphthalene
11 conversion and product selectivity over zeolite catalysts is reported. Subsequently, the effects of
12 modifying HY zeolite with different transition metals (Fe, Co, Ni and Cu) on the catalytic
13 isopropylation of naphthalene are presented.

29 **2. Experimental**

30 2.1. Chemicals

31 Naphthalene (99.7%) was purchased from Sigma-Aldrich, cyclohexane (99.6%) from Fisher
32 Scientific and isopropyl alcohol (99.6%) from Alfa-Aesar. Analytical grade of cobalt (II) nitrate and
33 iron (III) nitrate were purchased from Sigma-Aldrich. Copper (II) nitrate and nickel (II) nitrate were
34 purchased from Fisher Scientific. HY zeolite catalyst precursors (CBV 720, SiO₂/Al₂O₃=30) were
35 purchased from Zeolyst International as powder without binder and in the hydrogen form. Boehmite
36 (Pseudoboehmite, Pural SB[®]1) was supplied by Condea Chemie GmbH. Sodium carboxymethyl
37 cellulose (M.W. 90 kg mol⁻¹) and acetic acid (99.7%) were procured from Sigma-Aldrich. All
38 chemicals were used as purchased without further purification.

54 2.2. Catalyst preparation

55 The zeolite powder was converted into pellets in order to test their use in a fixed bed reactor. A
56 sample of HY zeolite (80 g) was sieved to 10 μm and added to boehmite (aluminum oxide hydroxide),
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1 carboxymethyl cellulose (CMC), acetic acid, and distilled water in the ratios of 30/10/3.7/100 in
2 weight, respectively. The mixture was kneaded to make a paste, and extruded into rods with 3 mm
3 diameter and 5 mm length using Instron 4467 Universal Testing Machine with 30 kN uniaxial
4 loading. The catalyst pellets were then dried at room temperature and calcined at 500 °C for 5 hours.
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6 Boehmite was used as a support, methylcellulose as a temporary binder and acetic acid was used as
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8 peptizing agent to improve the plasticity of the compounded batch for better extrusion characteristics
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10 [14, 15].
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15 Modification of zeolite was carried out by the wet impregnation method. In a 100 ml beaker, an
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17 appropriate amount of metal nitrate was dissolved in distilled water and stirred thoroughly until an
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19 uniform solution was obtained. Subsequently, powdered HY zeolite was sieved to 10 µm, added to the
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21 solution and stirred with a magnetic stirrer for 1 hour under heating at 60 °C. The ion exchanged
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23 zeolite was recovered by filtration and repeatedly washed with distilled water and pretreated at 70 °C
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25 in a vacuum oven overnight. The ion-exchanged zeolite was ground, meshed (210 µm) and calcined at
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27 500 °C for 3 hours. Catalyst pellets were prepared by the same procedure for manufacturing parent
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29 HY zeolite above.
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32 33 34 35 2.3. Catalyst characterisation 36

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38 Elemental analysis of catalysts was carried out by Bruker S8 Tiger X-Ray Fluorescence (XRF)
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40 spectrometer. The XRD pattern of all samples were recorded on EQUINOX 3000 X-Ray
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42 diffractometer with Cu K α_1 radiation source ($\lambda = 1.5406 \text{ \AA}$) in order to determine crystallite
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44 dimensions. Surface area measurements for pore size and volume were performed by the adsorption–
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46 desorption of N₂ at 77K using a Micromeritics ASAP 2010 instrument. Temperature Programmed
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48 Desorption of t-butylamine using Micromeritics AutoChem 2920 machine was used to measure the
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50 acidity of both parent catalyst (HY) and modified catalysts. A sample (10 mg) was placed in the U
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52 shaped quartz sample tube and pretreated in a helium stream (50 ml/min) at 500 °C for 1 h, then the
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54 temperature of sample was cooled down to 40 °C. Afterwards, t-butylamine was injected from a loop
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56 (0.54 cm³) to the sample tube for several times until the sample became saturated. Subsequently,
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1 under helium flow, the temperature of sample was increased from 40 °C to 150 °C and held for 1 h so
2 that all the physisorbed t-butylamine was removed. Eventually, the TPD profile was obtained from
3 150 to 600 °C at a heating rate of 10 °C/min [16]. The concentration of effluent stream was monitored
4 with a TCD detector and the areas under the peaks were integrated using GRAMS/32 software to
5 determine the amount of t-butylamine desorbed during TPD. Thermogravimetric analysis (TGA) of
6 the used catalysts was performed on a NETZSCH TG 209. A sample of coked catalyst (20 mg) was
7 placed in an Al₂O₃ crucible. Initially, under nitrogen flow, the temperature was increased to 150 °C
8 and held for 30 min to remove all the moisture from the sample. Subsequently, the temperature was
9 increased from 150 to 800 °C with a heating rate of 10 °C/min under nitrogen flow to remove soft
10 coke material. In the last step, the temperature was held for 30 min under air flow to remove hard
11 coke material.
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26 2.4. Dialkylation of naphthalene

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28 Dialkylation of naphthalene was carried out in a fixed bed reactor (i.d. 15mm, length 550mm) charged
29 with 2 g modified zeolite catalyst. The reaction mixture of naphthalene, isopropanol and cyclohexane
30 as solvent was introduced into the reactor from the top using a HPLC pump at constant flow rate of
31 0.8 ml min⁻¹. A schematic diagram of the rig is shown in Figure 1. The feed was preheated to reaction
32 temperature before entering the reactor. The reactor temperature (with an accuracy of ±2 °C) and
33 pressure (with an accuracy of ±1 bar) were maintained by a furnace and a back pressure regulator,
34 respectively. Nitrogen was used to purge the system before and after reaction. Initially, a blank run
35 was carried out using pellets manufactured from alumina without zeolite at typical reaction conditions
36 to make sure that no reaction occurred over alumina. The range of reaction conditions in the fixed bed
37 reactor were as follows: temperature 160-280 °C, pressure 1-50 bar, Weigh Hourly Space Velocity
38 (WHSV) 9.4-28.3 h⁻¹, isopropanol/naphthalene molar ratio of 1-6 and Time on Stream (TOS) 6 h.
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53 The liquid products were collected from the gas-liquid separator. Products were identified and
54 analyzed by using a GC-MS (Trace GC Ultra Gas Chromatograph with DSQ II Mass Spectrometer)
55 equipped with a FID detector and TR5-ms capillary column (15m x 0.25mm x 0.25, 0.25µm film
56 thickness). The analytical conditions were as follows: Column oven temperature program started with
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1 initial temperature of 100 °C for 2 min, heating up to 200°C by rate of 4°C/min maintained for 2
2 minutes, injection temperature and detector temperature of 250 °C, Carrier flow rate (He) of 1 ml/min,
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4 split ratio of 80 and injection volume of 0.1 µl.
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8 **3. Results and discussion**

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10 In section 3.1 the characterization of catalysts is presented in terms of acidity, XRD analysis, and
11 nitrogen adsorption-desorption measurements. In Section 3.2 the results of the isopropylation of
12 naphthalene are presented with regard to the effect of operating conditions such as temperature,
13 pressure, residence time and alcohol/naphthalene ratio. Thereafter the effect of modification of
14 zeolite catalysts with different cations is presented. The characterization results presented in this
15 section are used to help explain the observed effects in the isopropylation reactions.
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28 3.1. Characterisation of the catalysts

29 *3.1.1 Acidity measurement by Temperature Programmed Desorption*

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33 Acidity is an important factor for the alkylation of naphthalene and an optimum number of acidic
34 centers are required for a selective catalyst [6], [8] and [17]. Kamalakar et al. [13] stated that medium
35 or weak Brönsted acidic centers are required for selective formation of 2,6-DAN, however they
36 showed that a large amount of unwanted products, such as tri- and polyalkylated naphthalene are
37 observed due to the strong acidic centers present in the zeolite. Wang et al. [17] made a similar
38 observation; they found that 2,6-/2,7-DAN ratio was highly sensitive to changes in the number of
39 strong acid sites, and the moderate numbers of strong acid sites could be responsible for the
40 comparatively higher selectivity for 2,6-DAN. In other words, the key factor for higher selectivity is
41 not the total number of acid sites, but the number of moderate strength acid sites and the distribution
42 of internal channel surface catalytic sites (strong acid sites). In this work total acidity and acid
43 strength distribution were determined by Temperature Programmed Desorption (TPD) of t-butylamine
44 in the temperature range of 50-500 °C. The t-butylamine is a suitable base for TPD test as its high
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1 vapour pressure and its molecular structure do not have diffusional limitations in the microporous
2 zeolite and so it gives a more accurate measurement than the adsorption of ammonia [18]. It is well
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4 noted that strength of the acid sites can be related to the temperature that ammonia or alkyamines are
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6 desorbed from acidic centers [19, 20] and it can be categorized to weak, medium and strong acid sites
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8 when the desorption peaks are in the range of 150-250, 250-350, 350-450°C, respectively. Weak acid
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10 sites are due to surface hydroxyl groups, while trivalent aluminium in the framework structure is
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12 responsible for medium and strong Brönsted acid sites. The amounts of desorbed t-butylamine for
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14 acid sites on the parent and modified HY catalysts with different strength are listed in Table 1.
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20 3.1.2 XRD analysis

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22 The XRD patterns of parent and modified HY zeolites are shown in Figure 2. All samples exhibit the
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24 typical diffraction peaks of the faujasite (FAU) structure[21]. There are no amorphous phases detected
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26 in the pore structure and also metal ion modification has not destroyed the crystalline structure of the
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28 zeolite catalysts. Furthermore, no crystalline phases of metal ions were detected in modified samples.
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30 This implies that metal ions are finely dispersed at the cation sites of the zeolite making them
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32 undetectable by XRD [22]. The average crystallite size of samples were calculated by applying
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34 Scherrer equation on (300), (191), (170) and (222) XRD reflections [23]. Considering HY zeolite as a
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36 reference standard, the relative crystallinity of modified zeolites was determined according to the
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38 ASTM D3906-2003 method and is shown in Table 2. It can be seen that the relative crystallinity of
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40 Fe-HY, Ni-HY and Co-HY is higher than parent HY zeolite, which means that the impregnation of
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42 metals can increase the crystallinity of zeolite.
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49 3.1.3. N₂ adsorption-desorption isotherms

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51 Nitrogen adsorption-desorption at 77 K was used to determine the porosity, specific surface area and
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53 physisorption isotherms. Figure 3 shows the amount of nitrogen adsorbed versus different relative
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55 pressures for parent and modified HY zeolites. All samples exhibit a typical reversible type IV
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57 adsorption isotherm as defined by IUPAC [24]. The hysteresis loop is very similar to the H3 type
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1 adsorption isotherm with hysteresis characterisation. This trend at $P/P_0 > 0.4$ is due to capillary
2 condensation taking place in mesoporous structures. There is no limiting uptake observed over high
3 range of P/P_0 , which is characteristic of aggregates with plate-like particles [25]. Table 2 summarises
4 the properties of catalysts.
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8 The results show that Fe-HY has higher pore volume, while modification by Cu reduces the pore
9 volume by blocking the pore opening. Mingjin et al. [26] reported similar observations for the
10 modification of mordenite zeolite with copper. Due to the smaller ionic radius of Fe (0.64 Å) and Ni
11 (0.69 Å), impregnated metal ions can easily substitute into the zeolite lattice, while ions with larger
12 ionic radii (Co (0.72 Å) and Cu (0.72 Å)) resulted in lower pore volume [27]. It can be seen in Table 2
13 that BET surface area, pore volume and micropore area decrease in the order: Fe-HY>Ni-HY>Co-
14 HY>HY>Cu-HY while the pore size does not change significantly for the different catalysts.
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26 3.2. Isopropylation of naphthalene

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28 The effect of reaction conditions on the isopropylation of naphthalene over HY zeolite was
29 investigated by undertaking a series of reactions at varying temperature from 160 °C to 280 °C,
30 pressure from 1 bar to 50 bar, isopropanol/naphthalene molar ratio from 1 to 10, WHSV from 9.4 to
31 28.3 h⁻¹ for a time on stream of 6 hours.
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38 Naphthalene conversion and product distribution (IPN, DIPN and PIPN) as function of time are
39 shown in Figure 4. Naphthalene conversion is high and almost constant during the reaction time,
40 which indicated the high stability and activity of HY zeolite. IPN content in the product increased
41 slightly while the PIPN content decreased with time. This can be attributed to the deactivation and
42 poisoning of active sites during the reaction that decreased the acidic centers of zeolite and led to
43 decreased production of polyalkylated naphthalenes [13].
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54 3.2.1. Effect of temperature

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56 The effect of temperature on the reaction was investigated from 160 to 280 °C in increments of 20°C.
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58 Figure 5 shows the conversion and selectivity of HY zeolite at different reaction temperatures. It was
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1 observed that conversion of naphthalene decreased from 90 to 76% by increasing the temperature
2 from 160 to 280 °C. This implied that the catalyst deactivated after 6 h at elevated temperatures. The
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4 mol% of IPNs decreased from 46 to 30% by increasing the temperature from 160 to 200 °C, however
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6 this increased to 82% at 260 °C. This may be due to secondary reactions, such as trans-alkylation and
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8 de-alkylation of DIPN at elevated temperatures [28]. Selectivity to PIPNs was not changed
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10 significantly from 160 to 200 °C, but with an increase in temperature, this decreased from 35 to 4%.
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12 The DIPN content increased from 19% at 160 °C to 38% at 220 °C and then decreased to 14% at 280
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14 °C. This was attributed to the decomposition of PIPNs to DIPN and IPN at higher temperature, but at
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16 temperatures more than 220 °C, DIPN also starts to decompose to IPN.
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19 Figure 6 shows the schematic diagram of the reactions in the system proposed by Liu et al. [29]. They
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21 reported that, higher temperature favours secondary reactions such as dealkylation, disproportion,
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23 transalkylation, oligomerisation or polymerization of the different isomers. They pointed out that by
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25 increasing the temperature, these reactions occur in the following sequence: monoalkylation >
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27 dialkylation > isomerisation of dialkylated naphthalene > dealkylation ~ transalkylation ~
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29 disproportionation.
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33 The selectivity towards 2,6-DIPN was increased with an increase in temperature from 160 to 200 °C,
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35 and it remains almost constant at higher temperatures. Due to the higher energy barrier for 2,7-DIPN
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37 production (18 Kcal/mol) compared to 2,6-DIPN (4 Kcal/mol) [30], it can be concluded that higher
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39 energy is required for the isomerisation of 2,7-DIPN to 2,6-DIPN, which was enhanced with
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41 temperature. Based on the conversion of naphthalene and selectivity to DIPN, 220 °C was considered
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43 to be the optimum reaction temperature.
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46 47 48 49 *3.2.2. Effect of pressure*

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51 Figure 7 shows the conversion and product distribution after 6 hours for different pressures.
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53 Increasing the pressure from 1 to 50 bar decreased slightly the conversion of naphthalene from 86 to
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55 77%, while the ratio of 2,6-DIPN to 2,7-DIPN decreased from 3.0 to 2.8. When the pressure was
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57 increased from 1 to 35 bar, both IPN and DIPN decreased from 48 and 38% to 10 and 16%,
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1 respectively. PIPN was increased from 14 to 74%, but by further increasing the pressure from 35 to 50
2 bar, the trends were reversed. A selectivity of 22% DIPN and 22% IPN were observed at this pressure
3 (50 bar), while PIPN decreased to 56%. A significant contributing factor could be the change of the
4 reaction conditions from subcritical to supercritical conditions.
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8 In order to understand the product distribution the phase diagram of the fresh feed (naphthalene: 10
9 mmol, isopropanol: 40 mmol, cyclohexane: 300 ml) was calculated by Phase Envelope utility in
10 Aspen Hysys V7.1. Figure 8.a illustrates the phase diagram of the fresh feed. Calculated values for
11 critical pressure and critical temperature were 42 bar and 280 °C, respectively. Figure 8.b shows the
12 density and dynamic viscosity of the fresh feed at 280 °C as a function of pressure which was also
13 calculated by Aspen Hysys V7.1. It is clear (and expected) that the density and viscosity are very
14 pressure dependant in the region close to the critical point. The density and viscosity dramatically
15 increases at 42 bar.
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18 It can be concluded that changing the conditions from subcritical (35 bar) to supercritical (50 bar),
19 decreased the production of PIPNs and led to higher selectivity to IPN and DIPN. This could possibly
20 be due to the higher diffusivity (compared with liquid phase) and solubility (compared with gas
21 phase) exhibited in the supercritical region. Tiltscher and Hofmann [32] reported that by adjusting
22 pressure and temperature so that the reacting medium reaches the supercritical state, lighter
23 compounds (in this study IPN and DIPN) that deactivate the catalyst under subcritical conditions can
24 be stripped from the catalyst surface. In other words, in the supercritical region, it is easier for lighter
25 components (IPN and DIPN) to diffuse from the zeolite channels instead of being trapped in the
26 channels and converting to PIPN as a result of consecutive reactions.
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29 3.2.3. *Effect of residence time*

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31 The effect of space velocity (WHSV) on the conversion and product distribution was investigated,
32 from 9.4 to 28.3 h⁻¹. Figure 9 shows the conversion and product distribution over HY zeolite after 6
33 hours. Conversion of naphthalene was high in all conditions but by increasing the WHSV from 9.4 to
34 28.3 h⁻¹, the selectivity to IPN and DIPN was decreased from 68 and 42% to 32 and 27%,
35 respectively, while selectivity to PIPN was increased from 10 to 21%. Increasing the space velocity
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1 from 9.4 to 18.8 h⁻¹ increased the ratio of 2,6-DIPN to 2,7-DIPN from 2.7 to 3.0, which then
2 decreased to 2.8 by further increasing the WHSV to 28.3 h⁻¹.
3

4 The results indicated that at higher space velocity, non-shape selective reactions largely occurred on
5 the outer surface of catalyst rather than inside the pores, as it is assumed that the polyalkylation occurs
6 on catalytic acid centers located on the zeolite external surface [33, 34]. This can be attributed to
7 strong internal diffusion limitations inside the mesopores of the zeolite at higher space velocities (or
8 lower residence time), effecting reactant diffusion into the zeolite channels which would result in a
9 selective reaction. Based on selectivity to 2,6-DIPN, an optimum WHSV of 18.8 h⁻¹ was used for
10 further studies.
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22 *3.2.4. Effect of Alcohol to Naphthalene Ratio*

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24 Figure 10 shows the effect of isopropanol to naphthalene molar ratio on the conversion and product
25 distribution. Both conversion and selectivity were greatly influenced by changing the reactant ratio.
26 When the isopropanol content in the reactant mixture was increased from 1 to 4 (mol%), the
27 conversion increased from 77 to 86%. The selectivity to DIPN was increased from 23 to 38%, while
28 increasing the molar ratio drastically decreased the selectivity to IPN from 68 to 26%. Increasing the
29 ratio greater than 4 led to a reduction in content of DIPNs in the product. Moreover, with a molar ratio
30 of 4, the highest value of DIPN selectivity (38%) can be obtained. When the molar ratio was 2, the
31 lowest selectivity of PIPN (12%) was observed, whereas the highest selectivity of 3.5 to 2,6-DIPN
32 can be obtained with a 1 molar ratio.
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45 The increase in the isopropanol/naphthalene molar ratio led to a decrease in IPN concentration and an
46 increase in PIPN in the product mixture. This can be explained by the consecutive alkylation of IPN
47 by isopropanol to first DIPNs and then PIPNs. The decrease in naphthalene conversion at molar ratio
48 more than 4 is due to the deactivation of the catalyst by coking at higher space velocity.
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3.2.5. Modification of zeolite

Figure 11 shows the result of reactions of naphthalene with isopropanol over various modified zeolite catalysts after 6 hours time on stream. Modification of zeolite changed the catalyst activity from 77% for parent HY zeolite to 73, 76, 88 and 96% for zeolite modified with Fe(III), Co(II), Ni(II) and Cu(II), respectively. Modification of zeolite with Fe(III), Co(II), Ni(II) and Cu(II) increased the selectivity to IPN from 20% to 39, 32, 35% and 27%, respectively. No significant changes were observed for selectivity to DIPN in all samples. Selectivity to PIPN, which are coke precursors decreased from 56% for parent HY zeolite to 39, 45, 42 and 52%, respectively.

Table 1 lists the distribution of acidic sites for parent HY and modified zeolite. Desorption of *t*-butylamine in various temperature regions is indicative of the different acidic strength. During the TPD test on samples, three peaks at region of 150–250 °C, 250–350 °C and 350–450 °C were observed which corresponded to weak, medium and strong acid sites, respectively [12]. It can be seen that modification by transition metals not only can change the distribution of acidic centers but also can change the total acidity of the zeolite. For example, for the zeolite modified by Fe(III), strong acidic centers were decreased to 25% compared to the parent HY zeolite, while the medium acidic centers were increased to 43%. For zeolite modified by Co(II), a decrease in medium type acidic centers was observed, although, the total acidity was increased to 0.61 (mmol/g catalyst). Higher conversion of naphthalene over Co-HY and Cu-HY can be attributed to higher total acidity of these samples.

Wang et al. [17] have reported that the moderate numbers of strong acid sites are associated with higher selectivity for 2,6-DAN. The higher ratio of 2,6-/2,7-DIPN over Fe-HY zeolite can therefore be ascribed to lower strong acidic centers (25%). Meanwhile, higher selectivity to IPN over Co-HY and Ni-HY is due to a higher distribution of weak acid sites on these samples. Maheswari et al. [8] have reported that only weak and medium acidic sites are responsible for the initiation of mono-alkylation reactions.

The amount of coke deposited on the catalysts was measured by thermogravimetric analysis (TGA). Figure 12 illustrates TGA curve of coked zeolite catalysts after 6 hours. Each curve consists of three

1 steps: mass loss during the first step (150°C) is due to the removal of moisture from the samples. The
2 second step refers to the removal of soft coke at temperature 200-800°C under nitrogen flow. The
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4 third step corresponds to removal of hard coke at high temperature (800°C) and under air flow. The
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6 highest amount of coke was deposited on Co-HY (9.2%) and Cu-HY (8.7%) catalysts. This could be
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8 due to the higher total acidity of Co-HY (0.61 mmol/g cat.) and Cu-HY (0.49 mmol/g cat.) zeolite
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10 compared to the parent HY zeolite (0.43 mmol/g cat.). On the other hand, a higher amount of PIPN
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12 was produced on zeolite modified by Co and Cu. This confirms that PIPN molecules are possible coke
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14 precursors and therefore led to larger amount of coking on Co-HY and Cu-HY catalysts.
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17 A higher amount of coke was observed on zeolite modified by Co and Cu while less coke material
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19 was found on zeolite modified by Fe and Ni compared to parent HY zeolite (see Table 3). The higher
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21 amount of coke can be related to higher total acidity after modification (c. Table 1).
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26 **4. Conclusions**

27 Many efforts have been made to develop an environmentally benign, economically viable method
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29 with clear methodology for the selective alkylation of naphthalene over modified zeolites. In
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31 particular, modified Y zeolites were found to be promising catalysts for this goal. The effects of
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33 reaction conditions on the catalyst's activity and selectivity were studied and optimum conditions
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35 were reported. Maximum selectivity to DIPNs was achieved at 220 °C and 1 bar. The results of
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37 reaction at higher pressure proposed that PIPNs (which are coke precursors) are decreased in the
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39 supercritical region due to the higher diffusivity and solubility of the supercritical medium. An
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41 optimum WHSV of 18.8 h⁻¹ and an isopropanol/naphthalene molar ratio of 4 was found as the most
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43 suitable value. HY zeolite was modified by transition metals (Fe, Co, Ni and Cu) and was used for the
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45 dialkylation of naphthalene by isopropanol. It was found that modifying the zeolite significantly
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47 changed, not only the total acidity of the parent zeolite, but also the distribution of weak, medium and
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49 strong acid centers. Moreover, changes to the pore volume and BET surface area of modified samples
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51 are related to the ionic radius of the transition metal. It was observed that modification of zeolite by
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53 Co and Cu increased the total acidity of the zeolite, and therefore, less improvement of selectivity was
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55 observed on these catalysts. On the other hand, modification by Fe and Ni decreased the total acidity,
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1 and therefore better selectivity was observed on these catalysts. Among the catalysts tested for this
2 reaction, Fe-HY was found to be the best catalyst for a selective dialkylation of naphthalene with
3 optimum strength acidic centers and larger pore volume.
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9 **5. References**

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List of Figures and Tables

Table 1. Acidity of HY and modified zeolite measured by TPD of t-butylamine.

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Figure 1. Schematic diagram of the apparatus for dialkylation of naphthalene over modified zeolite;

Pump: HPLC pump for feed mixture. V1, V2, V3, V5 and V6: needle valves. V4 : back pressure regulators. T1, T2, and T3, thermocouples; P1, P2 and P3, pressure gauges; and RV1 and RV2, safety pressure relief valves.

Figure 2. XRD pattern of parent HY and modified zeolite.

Figure 3. Nitrogen adsorption-desorption isotherms of HY and modified zeolites

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Figure 8. a) Phase diagram of the fresh feed, b) Mass density and dynamic viscosity of fresh feed, naphthalene: 10 mmol, isopropanol: 40 mmol, cyclohexane: 300 ml, temperature: 280 °C

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Figure 11. Product distribution and naphthalene conversion over different zeolite catalysts, Reaction conditions: temperature: 220 °C, pressure: 50 bar, WHSV: 18.8 h⁻¹, isopropanol/naphthalene: molar ratio 4, TOS 6h

Figure 12. TGA profile of coked zeolite catalysts after 6 hours

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Table 1. Acidity of HY and modified zeolite measured by TPD of t-butylamine

| Catalyst name | Amount of desorbed t-butylamine (mmol/g catalyst) | | | Total acidity |
|---------------|---|-----------------------|-----------------------|---------------|
| | Weak ^(A) | Medium ^(B) | Strong ^(C) | |
| HY | 0.14 (34%) | 0.14 (33%) | 0.14 (33%) | 0.43 |
| Fe-HY | 0.13 (32%) | 0.18 (43%) | 0.10 (25%) | 0.41 |
| Co-HY | 0.22 (37%) | 0.18 (29%) | 0.21 (35%) | 0.61 |
| Ni-HY | 0.16 (38%) | 0.10 (25%) | 0.15 (37%) | 0.41 |
| Cu-HY | 0.14 (27%) | 0.19 (37%) | 0.17 (35%) | 0.49 |

Desorption temperature region: A = 150–250 °C; B = 250–350 °C; C = 350–450 °C

Table 2. Properties of zeolite catalysts

| Catalyst name | Amount of metal in zeolite (wt %) | BET surface area (m^2/g) | Crystal size (nm) | Crystallinity (%) | Pore size (\AA) | Pore volume (cm^3/g) | Micropore area (m^2/g) |
|---------------|-----------------------------------|--|-------------------|-------------------|----------------------------|--|--|
| HY | --- | 609 | 25.7 | 100 | 30.4 | 0.172 | 370 |
| Fe-HY | 2.3 | 762 | 29.3 | 139 | 31.7 | 0.212 | 457 |
| Co-HY | 1.6 | 641 | 33.0 | 59 | 30.7 | 0.182 | 393 |
| Ni-HY | 1.4 | 670 | 27.1 | 232 | 30.7 | 0.191 | 412 |
| Cu-HY | 1.5 | 584 | 30.8 | 228 | 31.5 | 0.161 | 348 |

Table 3. Coked deposition of used parent and modified HY zeolites

| Catalyst name | Soft Coke (wt%) | Hard Coke (wt%) | Total Coke (wt%) |
|---------------|-----------------|-----------------|------------------|
| HY | 5.9 | 1.8 | 7.7 |
| Fe-HY | 4.5 | 2.4 | 6.8 |
| Co-HY | 8.3 | 0.9 | 9.2 |
| Ni-HY | 3.8 | 2.9 | 6.7 |
| Cu-HY | 7.5 | 1.2 | 8.7 |

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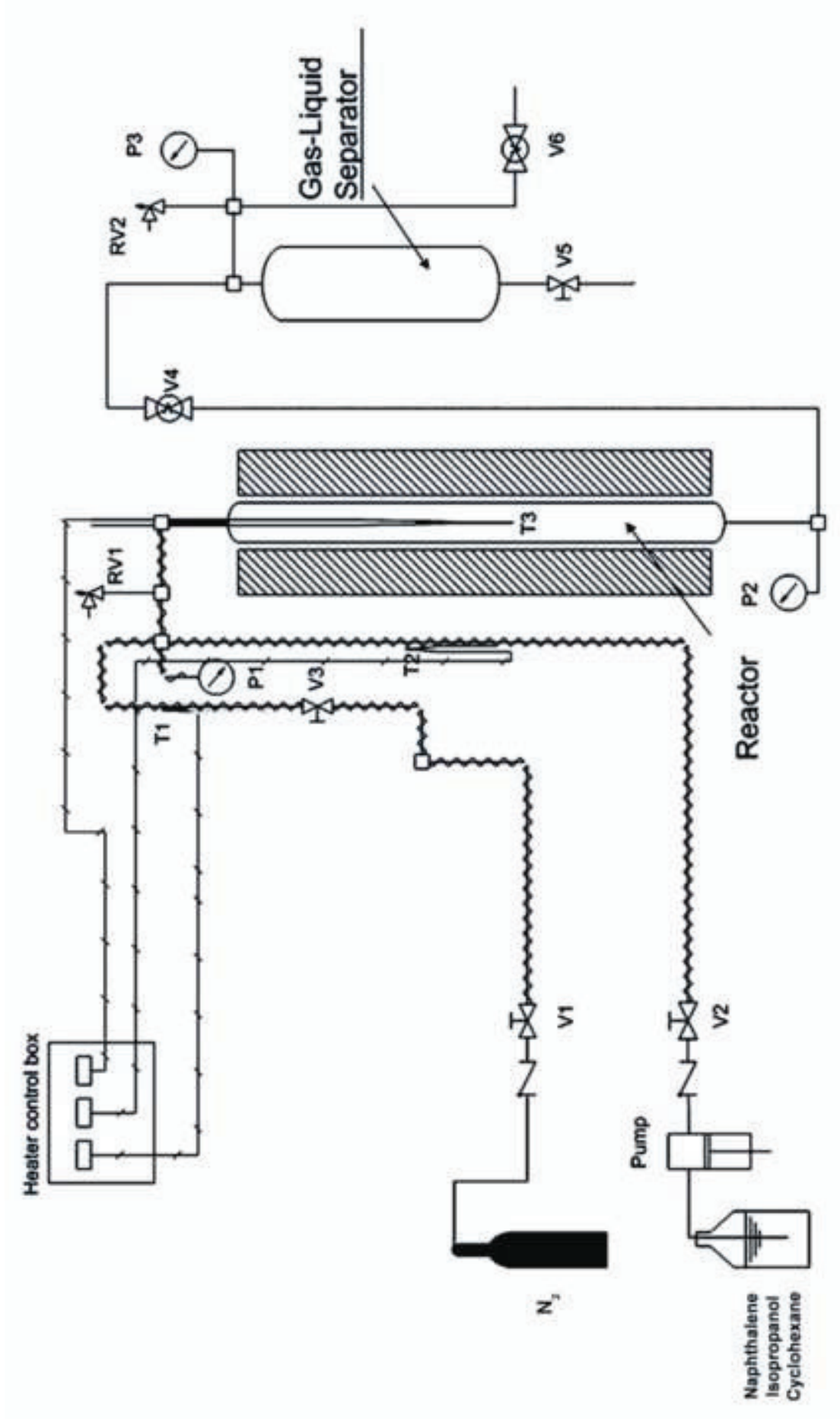


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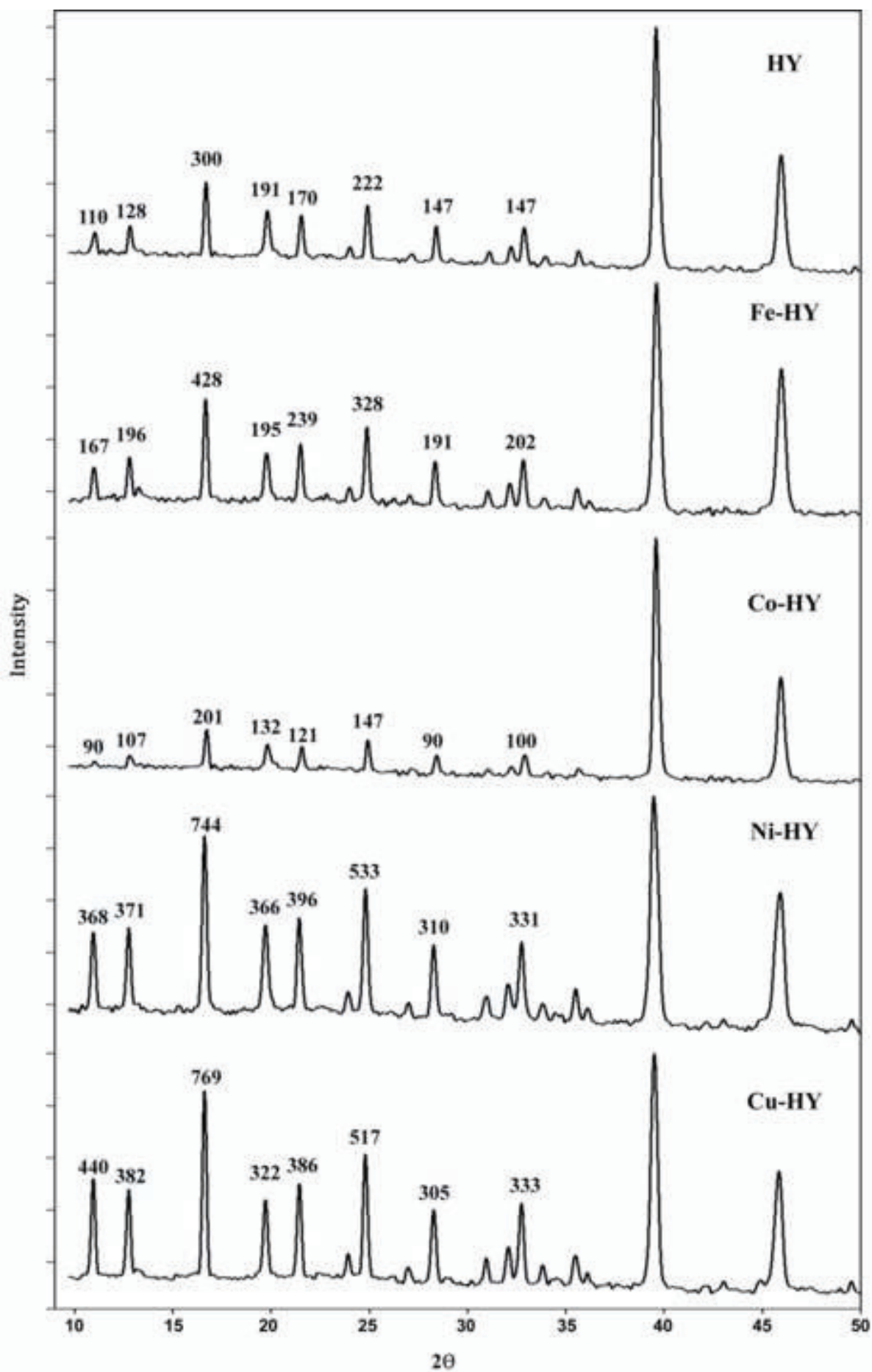


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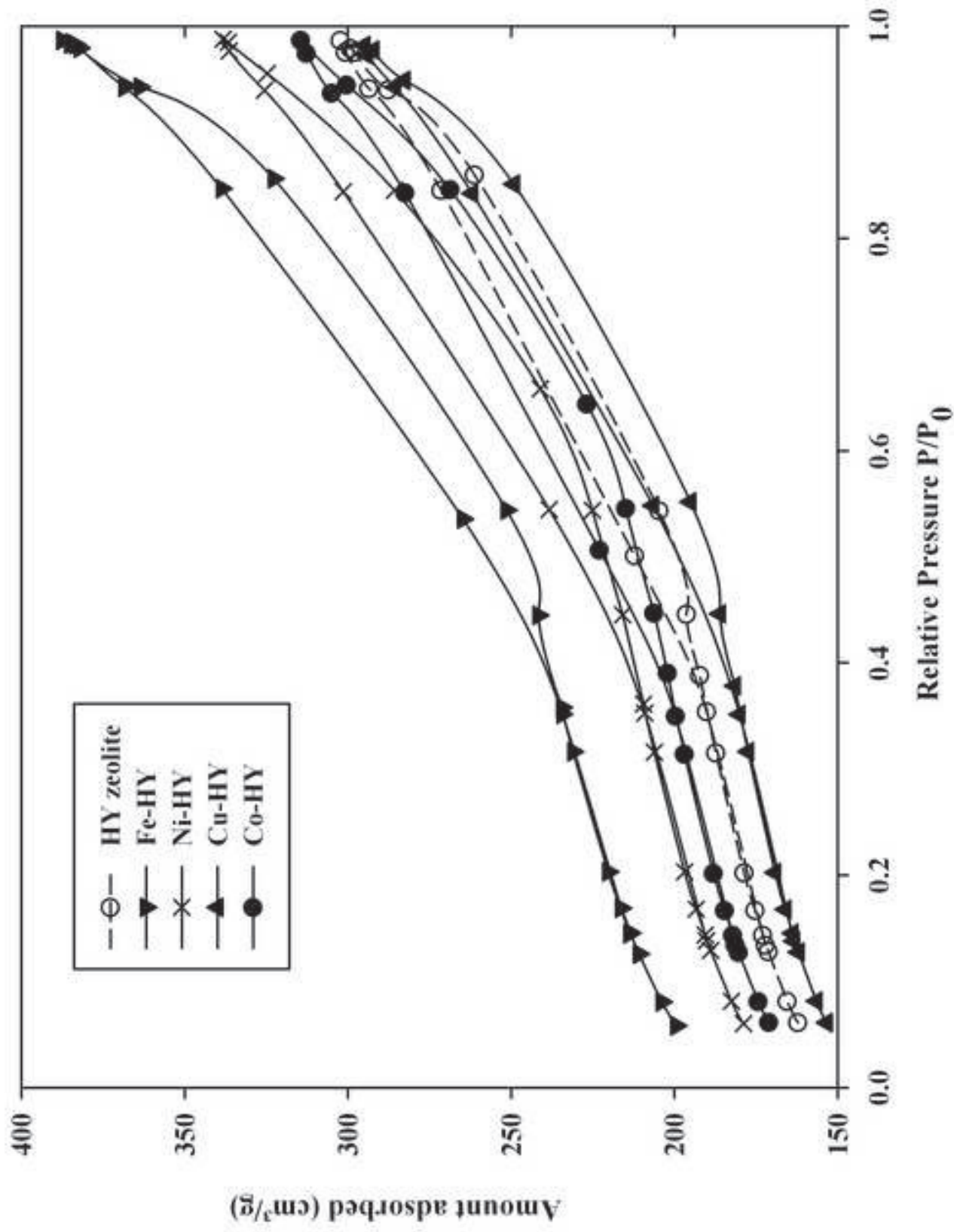


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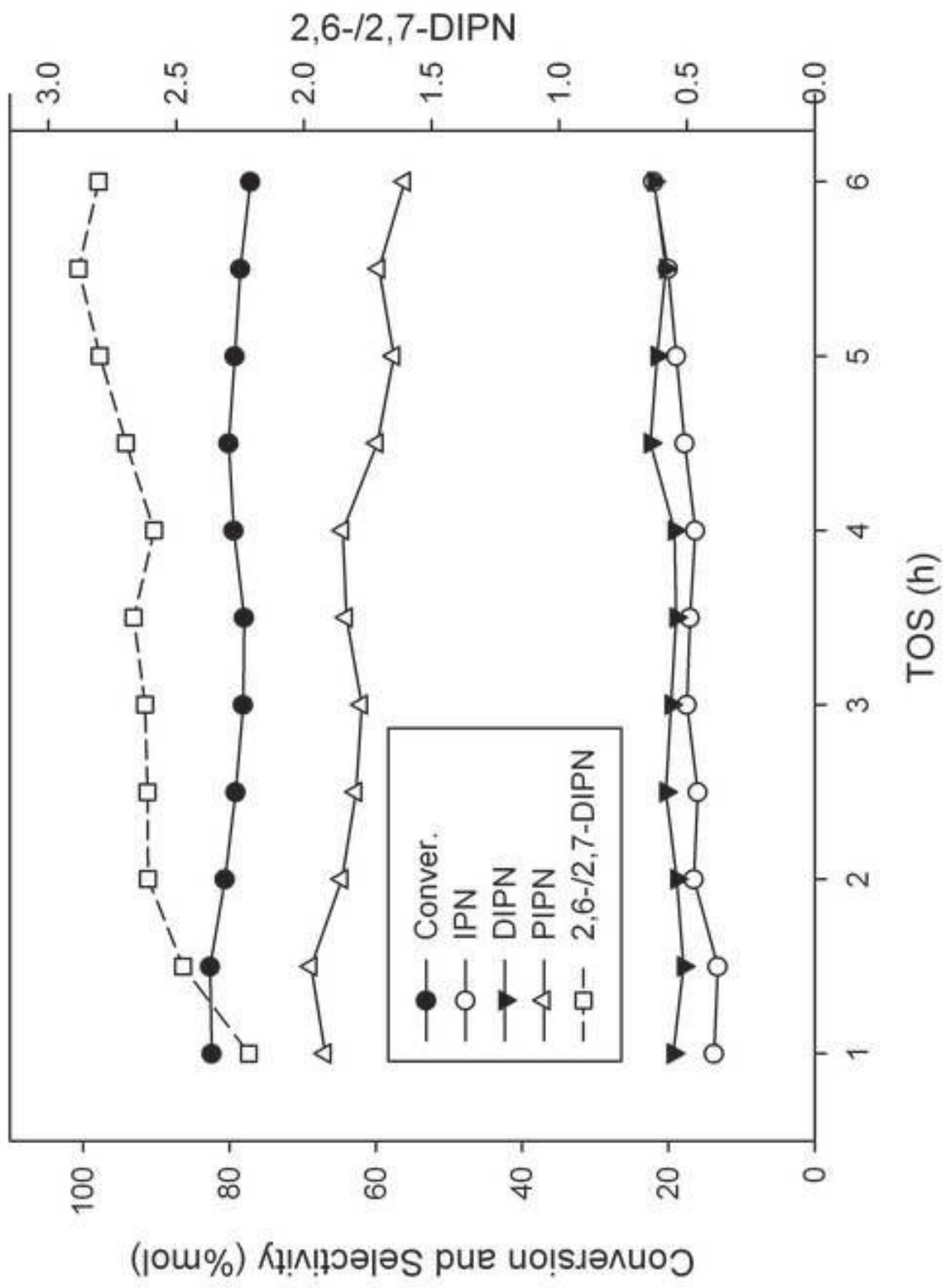


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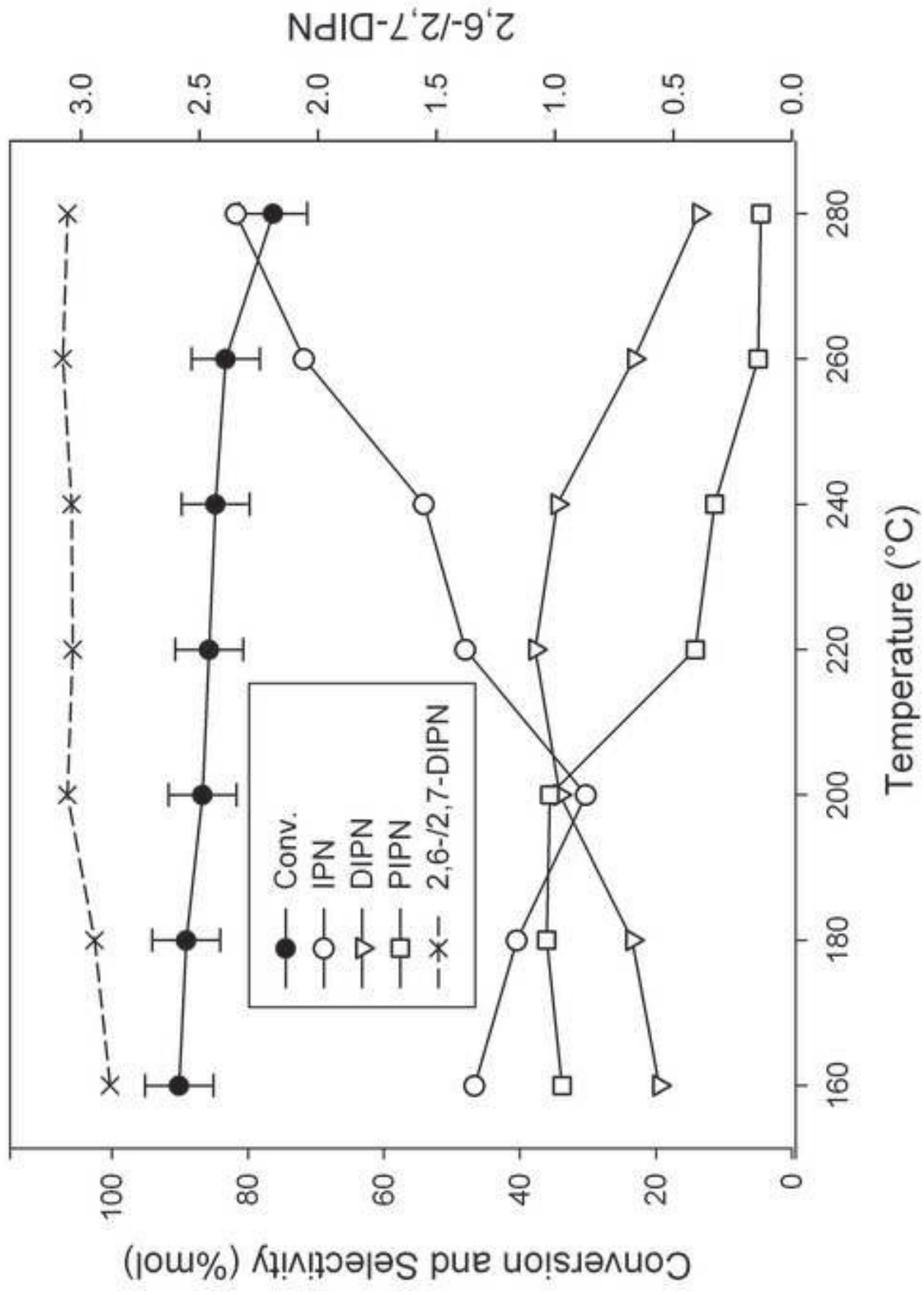


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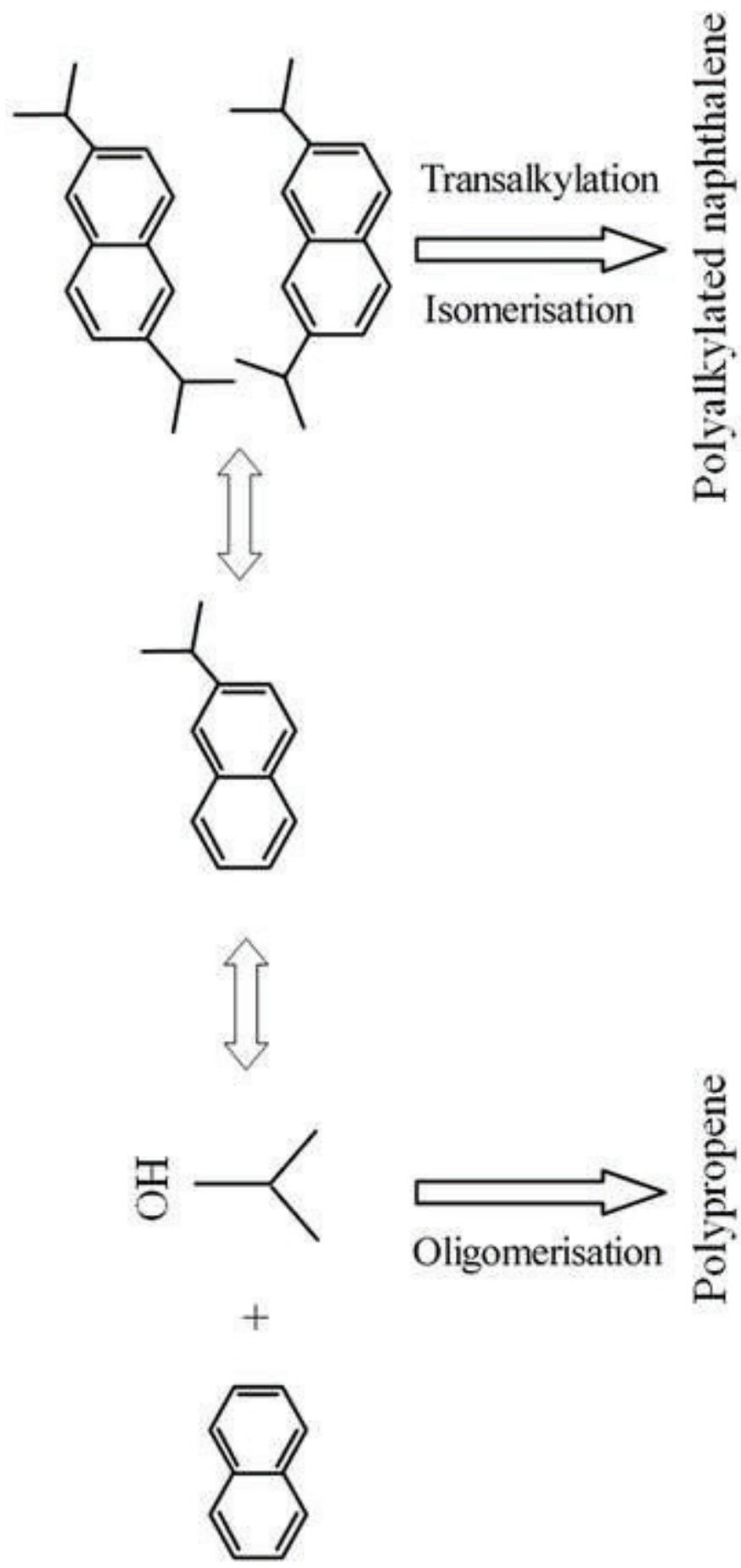


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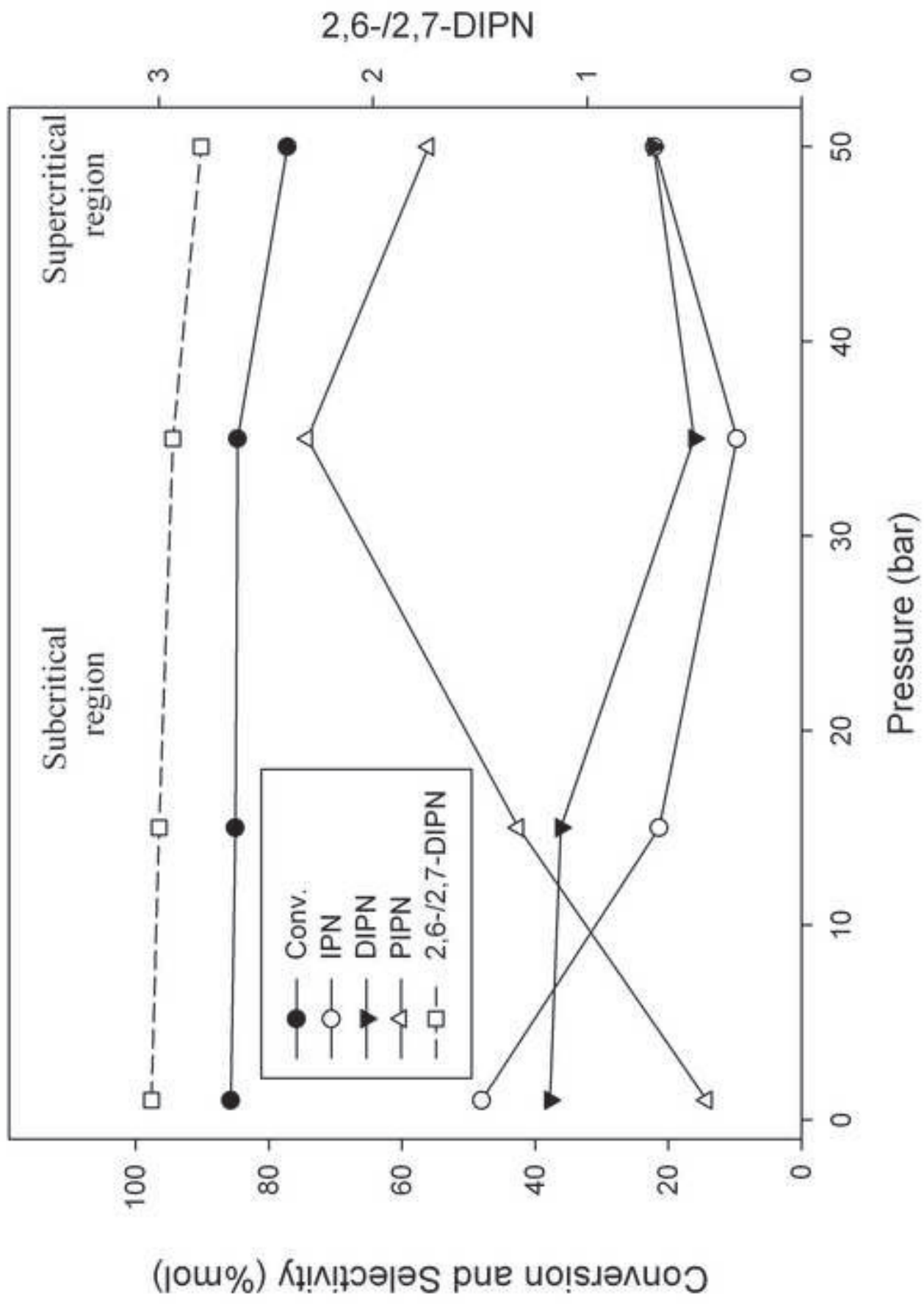


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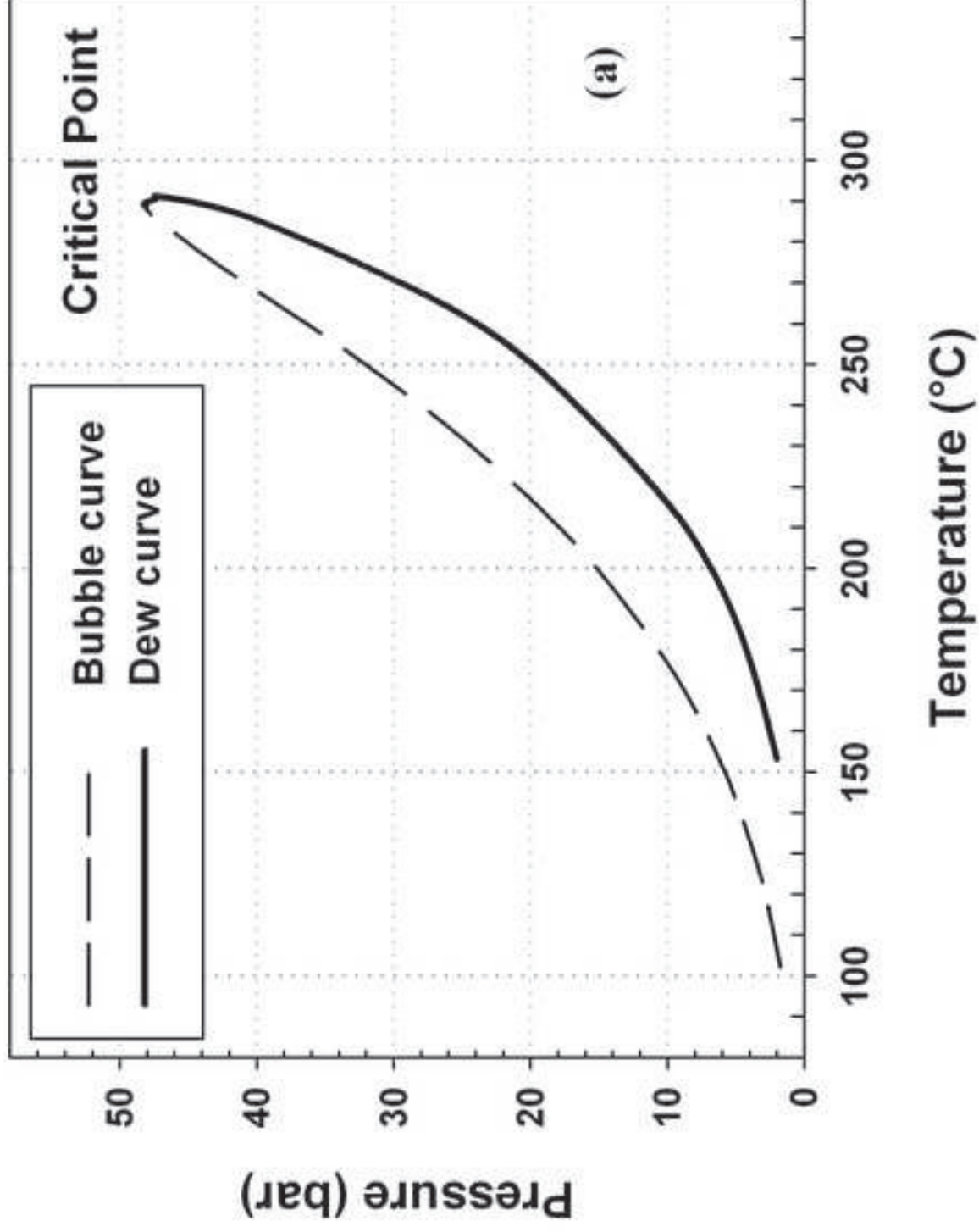


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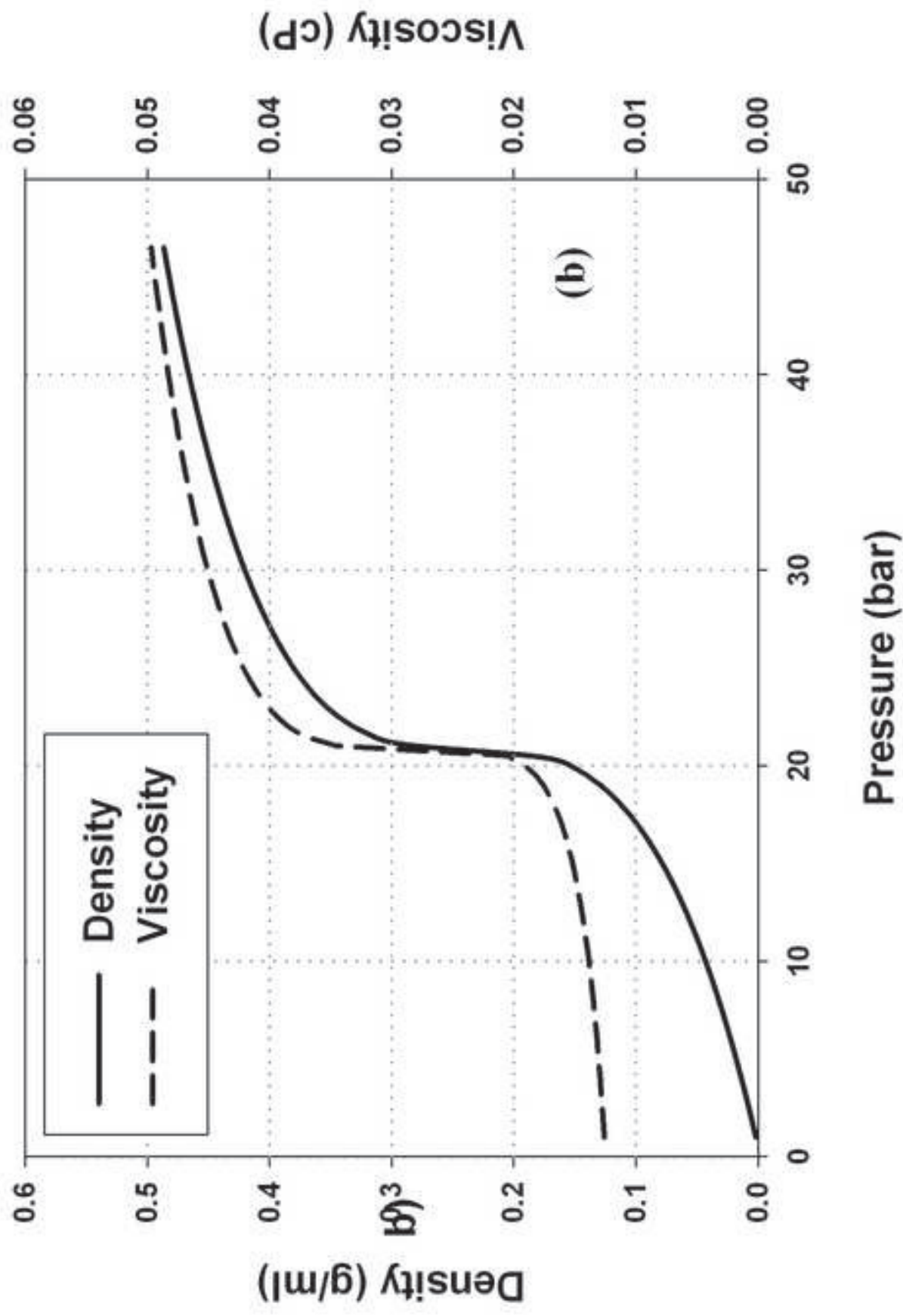


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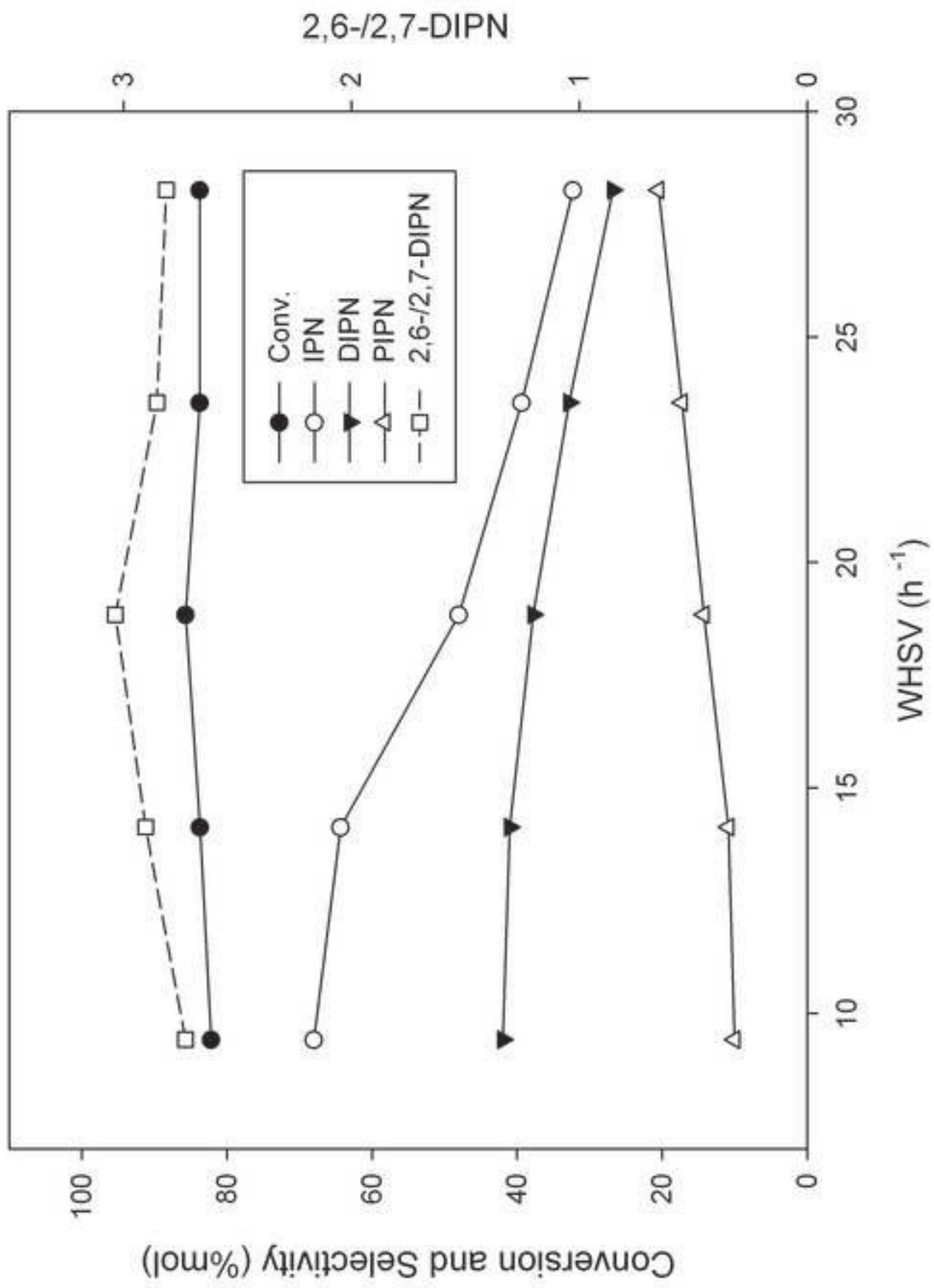


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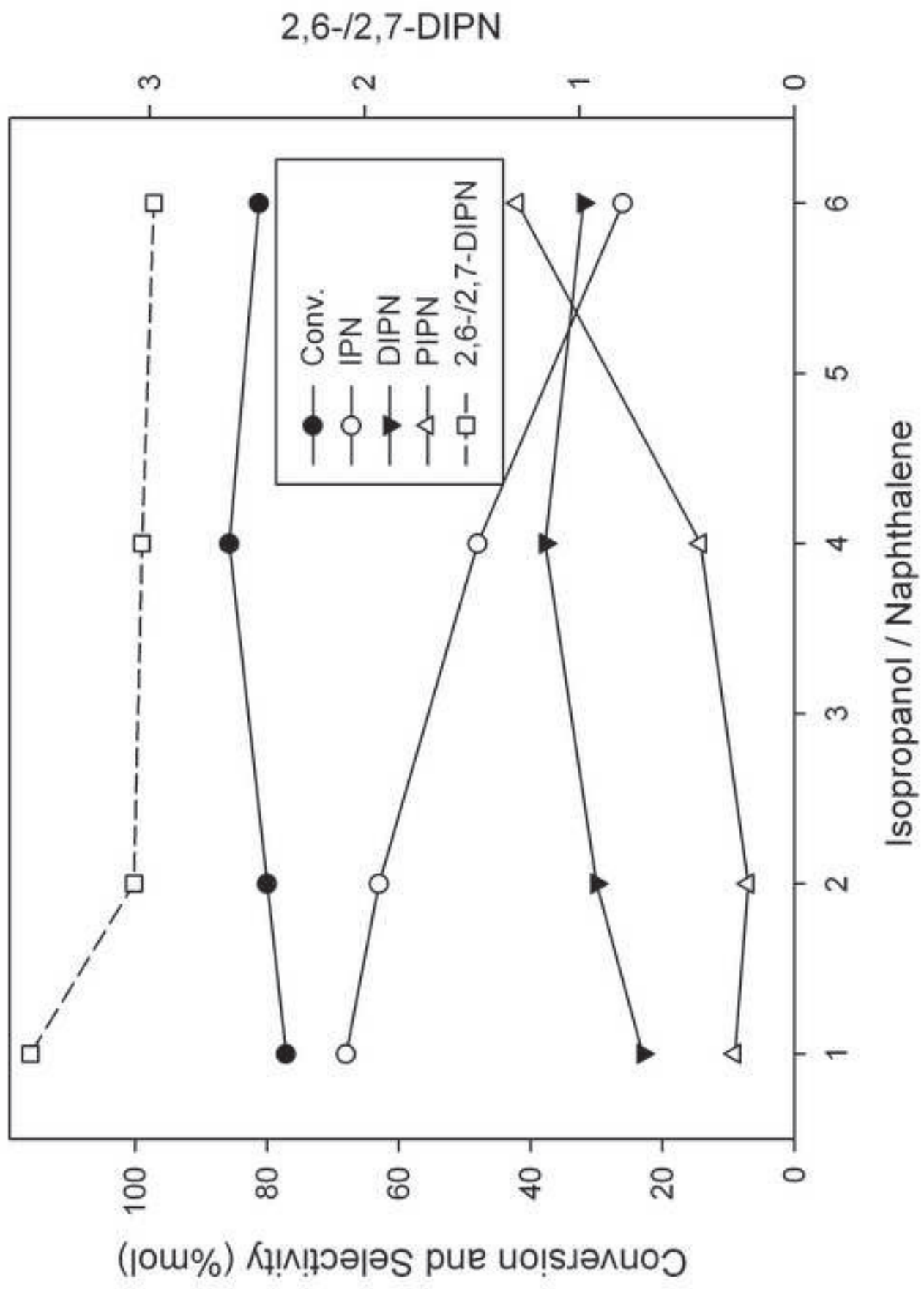


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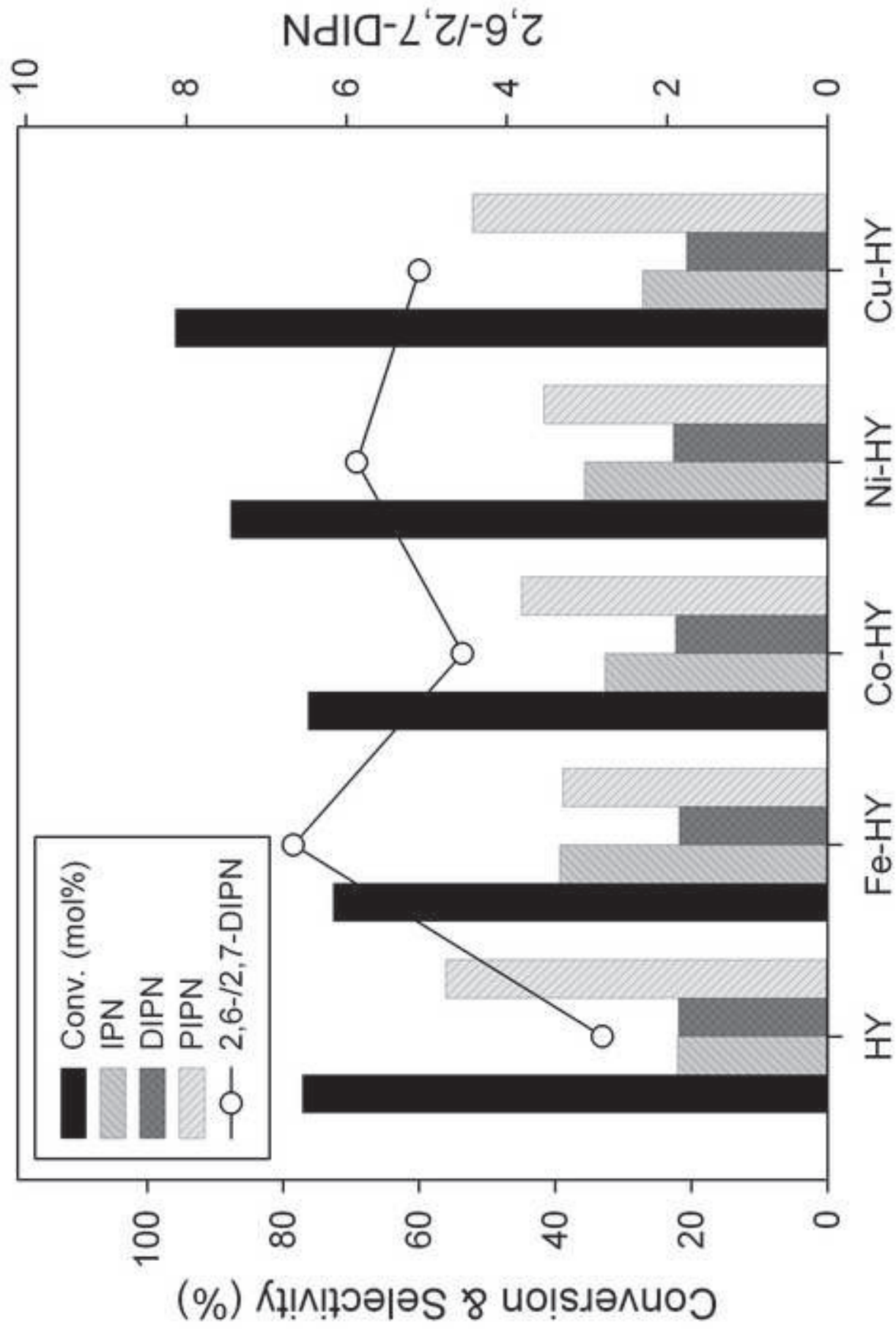
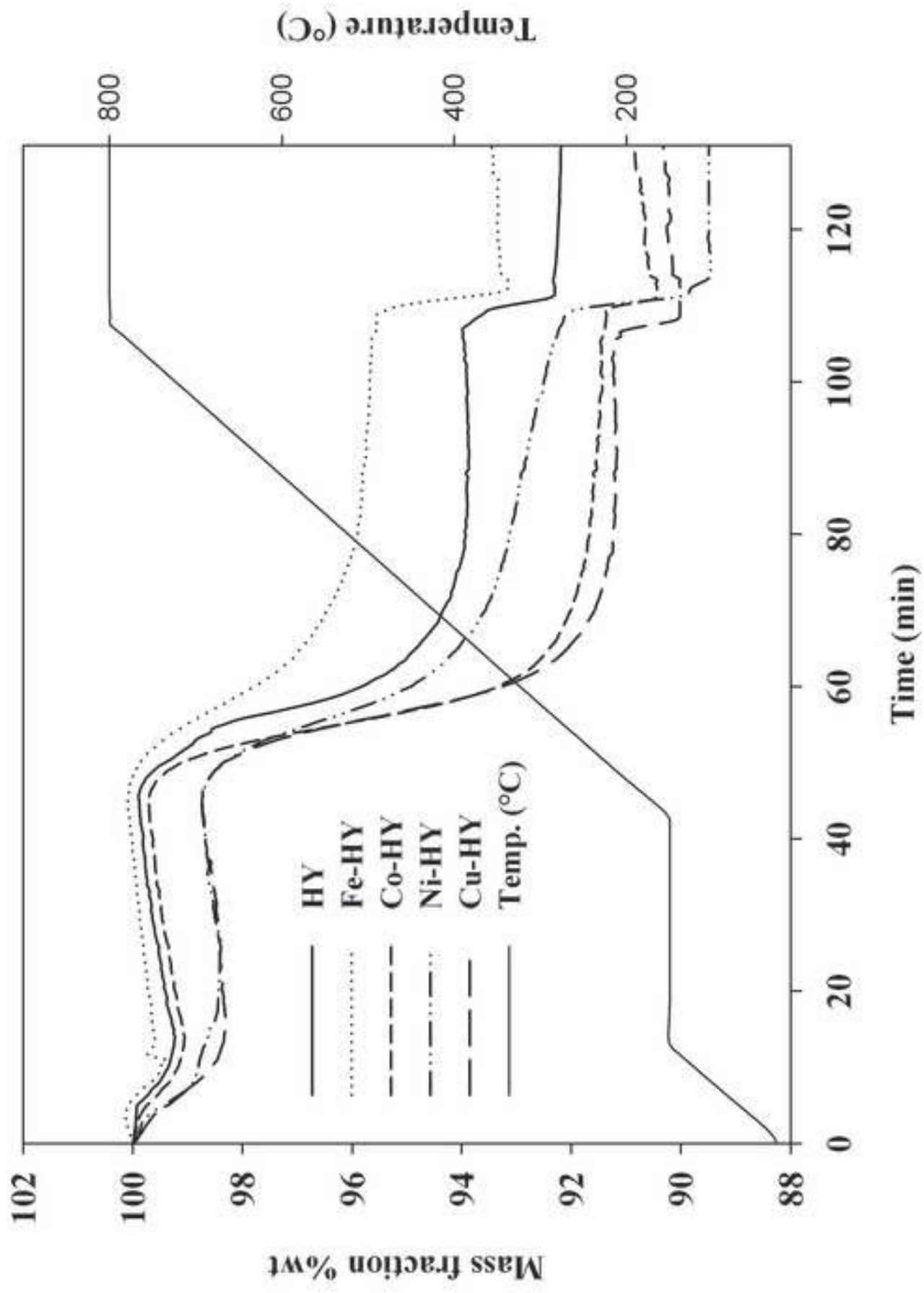


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