Hydrodenitrogenation of 2-methyl Quinoline - Effect of Steric Hindrance in Liquid Phase Catalytic Hydrogenation

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Abstract. Hydrodenitrogenation (HDN) of 2-methyl quinoline (quinaldine) and quinoline in liquid phase on S-NiMo/γ-Al₂O₃ catalyst was carried out in a batch reactor at 3.0 - 10.0 MPa and 130 – 360°C in Poly alpha-olefin solvent. Hydrogenolysis and Hydrogenation results in formation of products such as 1,2,3,4-tetra hydro Quinaldine (1-THQ), 5,6,7,8-tetra hydro Quinaldine (5-THQ), Deca hydro Quinaldine (DHQ), Butyl cyclohexane (BCH), Butyl cyclo hexene (BCHE) and butyl benzene (BB). Under studied condition, amine rings of quinaldine was rapidly hydrogenated and it forms relevant quasi equilibrium with 1,2,3,4-tetra hydro quinaldine (1-THQ), 5,6,7,8-tetra hydro quinaldine(5-THQ) and Deca hydro quinaldine (DHQ). The quinaldine reaction path either 1-THQ or 5-THQ indicated dependent of temperature and independent of partial pressure. Over which amine adsorption on metal sites reduced due to steric hindrance of methyl-group adjacent to N-bonding and increases the rate of intermediate formation through benzene ring hydrogenation. Distinguished HDN hydrogenolysis mechanism of quinaldine and its intermediate compounds were studied and compared with quinoline HDN. Thus, 5-THQ to DHQ and C-N cleavage identified as rate limiting step through steric hindrance HDN mechanism.

Keywords: hydrodenitrogenation, quinaldine, NiMo catalyst, heteroatom, hydrotreating

1. Introduction
For last 50 decades, the importance of hydro treating process for the removal of hetero atoms from middle and downstream distillates had increased in refineries. Hydro treating process had applied mainly in combined methodology for removal of sulfur, nitrogen and oxygen from petroleum fractions. Previously hydrodesulphurization (HDS) had long commercialization for removal of sulfur while mostly from aromatics. After 1970s, removal of nitrogen as hydro-denitrogenation (HDN) also recognized as an important part in heavy oil fuel processing. HDN consume higher stoichiometric H₂ amount than HDS due to saturation of rings and consuming H₂ to form NH₃ on intensive hydrogenation (HYD) [1-6], had interest in industries. The HYD of HDN was mainly based on the basicity of compounds, higher basic strength resulted lower HDN activity and vice versa [2-7]. The HYD of aromatics was totally depending on the position and strength of heteroatom bonding. Postulated HDN mechanisms of model compounds such as indoles, pyridines, quinoline and iso-quinoline have been summarized by few authors [2-10]. Also, number of studies has been reported on the steric effect of methyl groups on HDS model compounds such as thiophenes, benzothiophene and dibenzothiphene, but only few studies reported on HDN model compounds such as indoles and pyridines [11-17].

Quinoline HDN led to two intermediates formation, such as 1,2,3,4-tetra hydro quinoline (1-THQI) and 5,6,7,8-tetra hydro quinoline (5-THQI) in which HYD to 1-THQI was faster as compare to 5-THQI though equilibrium attained [4-18]. Also, HYD steps assessed first order but dependent on H₂ partial pressure, hydrogenolysis represented by lower-order reaction. HDN mechanism was favorable between 200 and 500°C with the rate limiting step depends on HYD mechanism, faster in rate and/or reach equilibrium thermodynamically under relative temperature in liquid medium [19-21]. Further literature study reveals that [22,23] the ideal condition for reaction network and kinetics of vapor phase quinoline under 3.5 to 7.0 Mpa pressure and 330 to 420°C. The secondary pathway of HDN was indicated that HYD followed with hydrogenolysis in C-N cleavage.

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Also, it confirmed that the possibility of dehydrogenated and abstraction of H from cyclic compounds among quinoline and its hydrogenated heterocyclic derivatives. In practice, the HDN level passes from 6 to 42 % by raising the temperature from 330 to 375°C. Here, few studies on investigation over indoles and alkyl-quinolines with NiO-MoO3/γ-Al2O3 catalyst (Ni-Mo) were noticed [14, 21]. Overall HDN conversion was generally higher when methyl groups (HDN activities of Methyl-substituted indoles) were on the benzene rings, but conversion lowered if methyl group on the N-ring [7]. Also, suggested CoMo/γ-Al2O3 was more active than Ni-Mo catalyst for vapor-phase condition of quinoline and yet to our knowledge, no steric hindrance study conducted with Ni-Mo in gas and liquid hydrogenation.

During the HDN study, the reaction at 340°C and 3.4 MPa, propyl benzene (PB) was low in final product composition with majority contains propyl cyclobenzene (PCB) [20-22]. In few cases, NiMo with Phosphorus enhance the HDN conversion, and also increase the electron donor capacity for the transition metals in HDN mechanism [20-22]. HDN of isoquinoline in 12 Mpa and 300 to 375°C with S-Ni-Mo/γ-Al2O3 showed 10 times faster than HDN of quinoline. HYD complicate for isoquinoline compare to quinolines was conclusion drawn [12]. Overview of above study revealed as that C-N cleavage mainly profound by N-ring HYD and alkyl substitution rather than benzene ring HYD [23-27]. Thus, double ringed heterocyclic model compound in such as quinoline, had very different aspects of mechanism as compared to methyl substituted (2nd position) N-ring. In such case methyl or ethyl substituted near N-heteroatom had steric hindrance influence over catalyst by reduce the rate of catalytic adsorption and dissociative. Also, it enhances the π-bonding from benzene over active sites and, restricts in N-bonding or lowered its binding strength which emphasized in dehydrogenation of benzene ring [27-28]. So far, the hydrogenation reactions consists of HDS, hydrodearomatization (HDA), hydrodemetallization (HDM) and HDN have mostly used catalytic systems of Ni or Co atoms promoted over MoS2 with γ-Al2O3-supported [24]. Also, in the HDN process, γ-Al2O3-supported had shown higher hydrogenolysis rate than other supported materials.

This investigation conducts HDN of 2-methyl quinoline (Quinaldine or Q) and rate of product formation with influence of NiMo catalytic behavior in site deactivation. In order to show the steric hindrance, the study was examining the product route in the reaction mechanism in Q HDN. Here, the parameters such as temperature and partial pressure were altered to verify the hydrogenation and hydrogenolysis rate.

2. Materials and methods

The solvent used in the experiments was a PAO2 (poly alpha-olefin) supplied by Nynas Naphthenics AB, Sweden, and the model compound studied were Quinoline (Ql) and 2-methylquinoline (Quinaldine or Q) (Aldrich) with purity of 98%. The feed mixture was pre-heated with solvent at 40°C, in order to get a homogenous solution and dropped into the reactor vessel. The employed NiMo/Al2O3 (NiMo-1) in this study was prepared by incipient wetness impregnation [22] of γ-Al2O3 with an aqueous solution of (NH4)6Mo7O24 (98 % purity from Aldrich) dried and calcined, followed with second step impregnation of Ni(NO3)2·6H2O (99 % purity from Aldrich) and H3PO4 (99% purity from Aldrich) resulted with specific surface area 157.6 m²/g and pore volume 0.34 cm³/g, and contained 13 % MoO3, 2.5 % NiO, 0.5% P and 84 % Al2O3. Catalyst was crushed and screened on a stainless steel screen (Haver & Boecker) to the size in the range of 10-30 DIN mesh number (German Unit) whose aperture was equivalent to 0.2-0.6 mm.

Also, a commercially manufactured HDN catalyst (NiO-MoO3/Al2O3) by Akzo Nobel (NiMo-2), under the trade name of Ketjenfines 840 (specific surface area = 189.7 m²/g and pore volume = 0.39 cm³/g), consists of 2.5 % Ni, 13 % Mo, and 84 % Al2O3 was used for HDN study. The catalysts (both NiMo-1 and NiMo-2) adsorption isotherm was represented in Figure 1. The catalyst activation were sulfidized at ambient pressure in a separate fixed-bed flow reactor, consisting of a 25 mm diameter glass tube placed vertically in an electric furnace and heated to a temperature of 400°C for 3 h under a mixture of 10 % by volume of H2S in H2, later catalyst was kept overnight under N2 flow. The desired nitrogen
concentration for all the test was set at 2000 ppm of nitrogen which means 2.05 wt% of quinaldine, quinoline and/or intermediates.

The experiment was conducted in semi-batch reactor of 300mL capacity build-in stainless steel. It was connected with H\(_2\) and N\(_2\) gas-line with sampling value in inlets and contains a separate outlet for flue gas. A process controller was connected with one to eight microprocessor-based temperature controller and magnetic stirrer at constant stirrer speed. The reactor was loaded with 150 mL of solution on 2000 ppm N in model compounds in Poly-\(\alpha\)-Olefin (PAO\(_2\)) that included a 1 g of defined amount of catalyst. During the catalyst activation, the catalyst was heated up to 400\(^\circ\)C and the temperature was kept for 2 h under a mixture of 10 % by volume of H\(_2\)S in H\(_2\). The catalyst was kept overnight under a small nitrogen flow.

Simulated distillation (ASTM D2887) was performed using a gas chromatograph (GC) technique (Perkin Elmer 5280) equipped with a packed column (10% silicon OV-101, 80-100 mesh, 1mx 1/8”x2.00mm) and a flame ionization detector (FID). The injector and detector were maintained at 250\(^\circ\)C and initial column temperature maintained at 40\(^\circ\)C and heated up to 300\(^\circ\)C at 16\(^\circ\)C/min. Final temperature was maintained for 16 min. A set of composite sample obtained over the temperature range of 270 to 360\(^\circ\)C in HDN of Q and 5,6,7,8-terta hydro quinaldine (5-THQ), was performed with a gas chromatographer (hp 6890 Series) equipped with a mass selective detector (hp 5973) in Nynas Petroleum AB, Sweden. Helium is used as a carrier gas at a flow rate of 1.2 mL/min. The column was a Factor Four Capillary Column (VF-5ms 30 M x 0.25 MM ID DF=0.25) (Varian). Initial temperature on the GC was 90\(^\circ\)C and this kept for 10 min. The temperature was raised 5\(^\circ\)C/min up to 300\(^\circ\)C and maintained for 10 minutes. The data recovered from the GC/MS (Gas Chromatographer/Mass Spectrometer) was scanned with the software coupled to the GC/MS; NIST Mass Spectral Database version 1.6. Signals from the GC/MS were integrated manually with ChemStation Software version B.01.00 (Agilent Technologies).

The concentration evaluated through area in GC, represented as sample in Figure 2, for intermediates was performed through Q and 5-THQ as reference compounds. Due to non-availability of response factor for ring-intermediates evaluation, the response factor of quinaldine was assumed for all the intermediates irrespective of near similar molecular weight and boiling points. By assuming the response factor of quinaldine, the deviation in data evaluation was estimated on the basis of Effective Carbon Number (ECN). The relative response factor of other intermediates on the basis of Q and 5-THQ, as reference compound, can be calculated on the basis of the ECN values. From this analysis, the response factor of the intermediates was in-range 0.943 and 1.056. The data evaluation was assumed on the basis.
of response factor of Q and/or 5-THQ, due to close molecular weight, ECN value and boiling point. The error in data evaluation is ±4.5 %.

Figure 2. Gas chromatogram technique (Perkin Elmer 5280) of the products of the 340°C (300 min) Quinaldine HDN

The specific area and pore volume of the samples were analyzed using Tristar 3000 automated Gas Adsorption Analyzer, measured by N\textsubscript{2} physisorption isotherms at -195°C. Approximately 1 g sample of catalyst was thermally dried in vacuum chamber at 90°C for 4 h in N\textsubscript{2} gas flow and used for specific surface area and pore-volume measurements. Hence, the characterization results were represented in Figure 1 and Table 1. The spent catalyst was refined in extracting the solvent through m-xylene for more than 22 h wash in Sohxlet apparatus. The refined spent catalyst was dried in vacuum dryer at 125°C under N\textsubscript{2} and analysis of coke deposition by BELAB AB, Sweden using an ASTM D 5291 standard test method (Leco CHN-600 instrument) was performed.

Table 1. Surface area characterization of catalyst used for HDN

| Material   | BET surface area [m\textsuperscript{2}g\textsuperscript{-1}] | Pore Volume [cm\textsuperscript{3}g\textsuperscript{-1}] | Average Pore Size [Å] | C [wt\%] |
|------------|----------------------------------------------------------|-------------------------------------------------------|------------------------|----------|
| γ-Al\textsubscript{2}O\textsubscript{3} | 199                                                      | 0.48                                                  | 97.6                   | 0.1      |
| NiMo-1     | 189.7                                                    | 0.39                                                  | 95.4                   | 0.09     |
| NiMo-2     | 157.6                                                    | 0.34                                                  | 87.06                  | 0.07     |

3. Results and discussions

The Q, 5-THQ and Q1 at 2000 ppmw N concentration in poly alpha-olefin (PAO\textsubscript{2}) solvent from base oil was tested in Batch reactor. With low feed concentration, 2.05 wt% had relatively low diffusion resistance over interfacial boundaries on liquid and solid phase. However, adsorption and desorption diffusion resistance considered as negligible. Here, reaction was mainly determined on catalytic surface reaction with pellet size below 10 mesh diameter. Feed was tested between 130 and 380°C, at range 3-10 MPa on 1 g of solid catalyst. The total conversion (HDN %) of HDN was considered as the ratio of total amount of N disappeared from initial concentration to initial concentration of 2000 ppmw N.

While examining temperature range between 130 and 210°C of feed, N-ring HYD mainly appeared in products, with conversion reach 96 % at residence time 180 min; Q hydrogenated to form 1,2,3,4-tetra hydro quinaldine (1-THQ), this conversion on different temperature condition was shown in Figure 3. Next on testing temperature between 240 and 270°C, there was significant formation of decahydro quinaldine (DHQ) with 1-THQ as intermediate. This increase operating temperature initiate HYD N-
ring, which indicate the N-ring HYD was mainly catalytic surface activity through N-inhibition. So, further increase in temperature, between 240 and 270°C, HDN results to form DHQ by benzene-ring HYD, as observed in Figure 4. Hence, rise in temperature above 300°C with above mentioned compounds, 5,6,7,8-terta hydro Quinaldine (5-THQ) and non-nitrogen compounds can be observed, as showed for different operating temperature like 300, 320, 340 and 360°C on HDN in Figure 4; that is, Butyl Benzene (BB), Butyl Cyclohexene (BCHE) and Butyl Cyclohexane (BCH) were final end product. However, by increase in temperature above 360°C resulted to cracking into lighter hydrocarbons, which consists of olefin and naphtha, which was not consider for further discussion.

Previous researches suggest that [3,10-13, 21] heteroatom’s electron donor strength influences the bonding formation such as covalent or ionic bonding. This strength involved with the acidic and basic nature of atoms. The study suggests that the basicity of 1-THQ was lower than Q; its N-bonding was stronger over the Lewis (Ni) or Bronsted (Mo) sites [20, 24, 26, 27]. HYD takes place by strong N-bonding and weak pi-bonding over N-rings. So, through two ways on 1-THQ, pi-bond and basicity, the bonding was stronger than quinaldine. The pathway, Q ↔ 1-THQ, was one of the fastest in this reaction network. Thus, previous research result confirms the formation of 1-THQl in quinoline have large rate constant value [6, 20, 21]. Here, HDN shows nucleophilic substitution on N-ring attained without any hindrance resist through low temperature. It might have the bonding with both position of pi and N, which can have both Lewis and Bronsted sites. But in both sites, the pi-bonding weak holding for short residence time to hydrogenates which could be a main reason for slow increase of DHQ concentration, as mentioned in Figure 4.
Figure 4. Graphical representation of intermediates concentration in quinaldine HDN on NiMo-1 at a)300°C, b)320°C, c)340°C and d)360°C on operating pressure Po=8.0 MPa (lines show to guide eyes)

At 300°C and 8 Mpa examined condition, initial hydrogenolysis in C-N cleavage begin through 1-THQ and DHQ pathway. BCH formed at higher operating temperature like 320°C and above. The sp² substitution on C-N position induces the path of BCH from DCH. It confirmed the pi-bonding existence in quinaldine over benzene group. Also high BB formation was not effective in HDN, which reduce the path in rate of formation of BCH. Thus BB concentration on decomposition was reasonably low as compare to BCH. The formation of BB was mainly C-N bond breakage from 1-THQ at higher thermal vibration impact in weaker bond energy while comparative in C-C bond energy. Thus, C-N breakage also induced by absence of pi-bond interaction on catalyst, which led to hydrogenate only amine group and, on other hand, deficient in population of H⁺ in electrophilic substitution reaction by donor H-S might retard the benzene-ring saturation. There was absence of 2-BA (intermediates of 1-THQ and BB) and 2-BHA (2-Butyl hexamine) (intermediate of DHQ and BCH) compounds in the product sample, which revealed that C-NH₂ bond detached at fastest rate to form NH₃ and BCH/BB. Here it can be estimate that ammonia had strong affinity, which attaches over active sites and due to hindrance by butyl chain at β-Carbon position readily detach itself, and free the molecule with donor H⁺ in gas phase. Inhibition of NH₃ is neglected as consider that active sites are occupied with S⁻ atoms on catalyst surface.

Table 2. Surface area characterization of catalyst used for HDN

| Material | P (MPa) | HDN (%) | 1-THQ (%) | 5-THQ (%) | DHQ (%) | BB (%) | BCH (%) | BCH+ (%) | 5-THQ / 1-THQ |
|----------|---------|---------|-----------|-----------|---------|--------|---------|----------|---------------|
| NiMo-1   | 3       | 83.9    | 16.1      | 40.3      | 33.4    | 3.6    | 1.7     | 3.5      | 1.3          |
|          | 8       | 91.5    | 8.5       | 55.2      | 11.8    | 11.0   | 1.9     | 11.6     | 0.0          |
| NiMo-2   | 3       | 87.9    | 12.1      | 46.2      | 31.1    | 3.8    | 2.1     | 3.5      | 1.3          |
|          | 8       | 91.2    | 8.8       | 54.6      | 11.6    | 11.0   | 2.0     | 12.0     | 0.1          |
| γ-Al₂O₃  | 3       | 70.5    | 29.5      | 38.8      | 22.5    | 5.0    | 0.8     | 1.9      | 1.5          |
|          | 8       | 70.5    | 29.5      | 38.8      | 22.5    | 5.0    | 0.8     | 1.9      | 1.5          |

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Table 3. Results of HDN of Quinoline (Ql) at 320 °C (residence time = 60 min)

| Material    | P (MPa) | HDN (%) | Product Composition (mol %) | 5-THQI / 1-THQI |
|-------------|---------|---------|----------------------------|------------------|
| NiMo-1      | 3       | 92.6    | 7.4 63.6 6.5 13.9 1.7 6.6 0.3 | 0.1              |
| NiMo-2      | 3       | 92.5    | 7.5 63.1 6.2 14.4 1.8 6.8 0.2 | 0.1              |
| γ-Al2O3     | 3       | 83.5    | 16.5 70.3 6.5 3.9 0.9 1.9 0  | 0.1              |

Elevated partial pressure of H₂ on 340°C of HDN Q and Ql were investigated to observe intermediates formation. The formation of 5-THQ concentration increased 4 to 6 times higher with respect of 1-THQ during lower partial pressure 3.0 Mpa. Figure 5, Table 2 and 3 shows the increase in weight fraction (wf) of 5-THQ confirms for both NiMo-1 and NiMo-2, which explains that 5-THQ formed highest at 3.0 MPa. The results in Figure 5 shows that increase in partial pressure from 3 to 10 MPa at 340°C, 5-THQ suppressed with limiting formation and on counter relation, thus concentration of 1-THQ increases rapidly. In Figure 5, showed 5-THQ wf reached 0.15 in 30 min residence time and maintained constant for rest of the period for 8 MPa. However 3 MPa gave high concentration of 5-THQ reaches 0.6 wf in 90 min residence time and increases in concentration steadily maintained between 0.6 to 0.65 wf after 90 min for longer residence time. It was noticed that the concentration of 5-THQ relatively stable after certain residence time for lower partial pressure, which exerted equilibrium with other intermediates. To compare the quinoline HDN, referred to Table 2 and 3, the HDN conversion was 92.6 % as of Quinaldine converted only 82.7 % at 3.0 Mpa. Also, the concentration of 5-THQ was higher with respect to 5-THQI at same condition. Q1 to PB and PCH for both NiMo-1 and NiMo-2 performed relatively similar conversion.

Figure 5. Graphical representation of 5-THQ, 1-THQ and DHQ concentration from quinaldine HDN on NiMo-1 for 340°C at different operating pressure range as 3.0, 4.5, 6.3, 8.0 & 10.0 MPa, a) wt fraction of 5-THQ appeared, b) wt fraction of 1-THQ (solid lines) and DHQ (dotted lines) appeared in product sample (lines show to guide eyes).

The probability of low H₂ partial pressure creates the diffusion resistance on interface at gas-liquid and gas solid interfaces, and relative in H₂ occupant reduction on distribution over catalyst active sites. With deficient H₂ could direct in two way reaction mechanism; first in relative to higher vacant sites with no H⁺ were offered by metal-S-N and/or pi-bonding which induced in increase of H-abstraction from solvent olefin group, hence it undergo HYD of benzene ring or amine rings, and second partial HYD of benzene and amine group with limited H₂ on active sites rearrange on delocalization mechanism over amine group by dragging from benzene group, respectively. However, at below 350°C in subject...
of liquid hydrogenation, we assume that the possibility of H-abstraction from olefin and H₂ gas-phase through gas-liquid interface were equally contributing for HYD. This also implemented in vise versa for DHQ which increases for higher partial pressure. Also, possibility of steric hindrance over methyl group inherently affects the N-bond which relatively resists hydrogenating amine-ring with respect of pi-bonding on catalyst. Thus, the mobility of H₂ from active sites restricted over benzene-ring saturation. Higher concentration of 5-THQ, during low partial pressure, was evident over steric hindrance effect of methyl group over heteroatom on amine-ring. The rate of 5-THQ formation increases on higher temperature i.e. above 270°C. Also, the product selectivity 5-THQ reached equilibrium at certain concentration and stays constant on contact time. Selectivity was in terms of the ratio of individual products to the total sum of 1-THQ, 5-THQ and BCH, which were the major species formed in samples. 5-THQ was mostly accumulating in solvent with less probability in converting into DHQ at higher than 300°C. Hence, this might be due to the weaken binding over N and S. Generally, 5-THQ formed through pi-bond on catalyst. So, here it might be due to the pi-position approach towards Lewis site. But, it was only confirmed through the behavior of 5-THQ testing at above discussed temperature. Around 360°C, the conversion of 5-THQ seemed to be lowered slowly. Also, in relation with benzene-ring hydrogenation at 320°C, pi-bonding had less effect over catalytic sites in prior to thermal decomposition. One such identity to find steric hindrance can be in estimating BB rate of formation with subject to catalytic bonding and thermal vibration of C-N. Thus, literature proved that thermal vibration had influence in relation to weak bonding strength with bond energy of 130 kJ/mole [5, 6, 13].

By C-N breakage, elimination reaction involved in NH₃ detachment at faster rate-step as explained in previous section. However, it can be estimate that NH₃ has strong affinity, which attaches over active sites and due to hindrance by butyl chain at β-Carbon position, leads to increase the rate of product formation such as BB, BCH and BCHE. The result revealed that higher order increase in BB with respect of temperature, and for increase in H₂ partial pressure, it had inclination over reactant concentration. The results were comparable and shown in Figure 2 and 4. Here, it confirmed that BB formation depends on temperature and reversible pathway can be identified with the slight decrease in formed BB for different partial pressure.

By examining 1-THQ HDN, it represent that the complete HYD of benzene and amine-rings into DHQ, but it was resist to form 100 % conversion from 1-THQ. It approached up to 40 mol/g, and started to convert products as BB. Suggestion over equilibrium attained with DHQ might have the bonding with position of pi and N-ring over flat position respective to catalyst surface, which can have both Lewis and Bronsted sites. However, in both sites, the pi-bonding was weak and doesn’t involve higher rate of hydrogenation. This could be the reason for slow formation of DHQ and higher in BB. Generally, the pi-position bonding on Ni-S sites and N-position with Mo-S sites, as demonstrated by DFT Theory on promoter and catalytic sites identification [11], the formation of DHQ results in maximum conversion.

Initially, the lower temperature hydrogenation at 5-THQ HDN was studied as such with concentration 2000 N-ppm in Poly α-olefin solvent. At 180-240°C, there was no sign of any other compound except traces of Q and 1-THQ. The hydrogenation had completely depends on the catalytic activity, which have complete conversion at 270°C and 300°C (Figure 6). These proved the strong bonding nature at Lewis sites of catalyst by N. Research studies referred that both Ni and Mo sites are equally participating for N-bonding and actively involve for products formation [21,22]. Also investigation of benzene ring HYD had covered in later part of our research study.
5-THQ HDN was studied at elevated H₂ partial pressure and temperature 270-360°C. HYD of 5-THQ undergo 60% conversion into DHQ at 320°C on 90 min residence time. Further increase in residence time results in formation of 2-BCHA and BCH. Similarly, at 360°C, formation of DHQ, Q, 1-THQ and BCH were appeared. The heterocyclic 5-THQ was hydrogenated to DHQ followed by ring opening to 2-Butylcycloaniline (2-BCHA) and BCH. This was subsequently dehydrogenated into two different forms. Firstly, 2-BCHA to BCH, and secondly, 2-BCHA to 1-Butylcyclohexene (1-BCH), and this could also arrived from BCH or Butylbenzene (BB) through respective rate of dehydrogenation. As, it discussed before, that the rate determining step was influenced by ring opening of DHQ.

In parallel sequence of 5-THQ HYD, this dehydrogenated resulted to quasi equilibrium with Q. Also hydrogenated 1-THQ followed by CN cleavage into 2-Butylbenzamine (2-BBA) could be one more reaction path. 2-BBA subsequently hydrogenated to 2-BCHA, and the NH₃ split from 2-BCHA by elimination step at the faster rate. Here, it was predicated that the rate determining step could be hydrogenation of 2-BCHA to 2-Butylcyclohexyamine. BCH formation as end product appeared from HDN of Q derivatives. This product formed by HYD of both benzene rings from BB or DHQ through 1-THQ. In overview, the HYD of N-ring after benzene-ring saturation seemed as slow mechanism. Also, the respective end product of 1-THQ and 5-THQ, as represented in Figure 6, were BB and BCH. While rate of HYD of 5-THQ was slower than 1-THQ, because 5-THQ was linearly raising respect to time. From this result understanding and concentration of intermediates, dehydrogenation of DHQ to 5-THQ was faster than the dehydrogenation of 5-THQ to Q, which considered as slowest step. Breakage of the C-N bond of the saturated heterocyclic ring from 1-THQ to give 2-BBA was relatively one of slowest irreversible step. With decorated Ni atoms over the MoS/Al₂O₃, the activity is enhanced with the indicating the Ni-promoting effect have high effect to increase the path of 5-THQ. Also, the investigation on MoO₃-derived metallic catalyst has 4-times lower hydrogenation rate without promoter effect [24].
The study limits to the identification of steric hindrance effect in the reaction pathway and further related with the influence of bimetallic effect over the mechanism are not investigated.

We demonstrate with BB HYD to identify the hydrogenation in forming of two main products: BCHE and BCH. The concentration of each compound formation represented with respect to BB concentration and temperature. Here, for a 320°C and 2.0 MPa, concentration of BCH relatively depends on BCHE concentration, but BB holds constant throughout as shown in Figure 6. Most of the BB was considerably converted into BCHE and BCH during heat-up. The formation of BB was mainly C-N bond breakage in 1-THQ. This is due to the weak bonding of pi-position on catalyst, which hydrogenate and C-N breakage at amine-ring. After breakage, elimination reaction was undergone to remove ammonia through fast step. Here it could be possible that ammonia (N) has strong affinity, which attached over active sites and due to hindrance by butyl chain at β-Carbon position at 320°C, leads to gas phase product. So, there was no deduction of compounds like 2-BA and 2-BHA (2-Butyl hexamine) in the product, which confirm inhibition of NH₃ negligible and detach from site much faster rate. At different operating temperature, BB increased at linear rate and significantly small effect for different pressure condition. Hence, BB had similar formation rate from all tested intermediates and feed, which was observed in Figure 6.

The formation of BCH was the desired product in HDN of quinaldine derivatives. The result in Figure 6 confirms that BCH formation indicated by HYD of BB with BCHE as intermediates. As most of BB HYD during heat, there was slight decrease in concentration of BCH and raise in BCHE in Figure 6 for above 300°C. In which, it confirmed that BCHE and BCH were temperature dependent equilibrium mechanism. From our study, BCH shows highest concentration in term rate of formation for both elevated temperature and pressure conditions, respectively. This was confirmed in the Figure 2 and 3. The active sites bonding of both pi- and N position by reactant ingredient the BCH formation. So, it confirms the pi-bonding existence in quinaldine to catalytic sites as strong as amine-bonding.

However, kinetic study in literature [13, 20, 22] confirmed the magnitude of rate constant of DHQ to BCH was higher than Q to 1-THQ. Also, some researches indicated [7, 13, 15] that Q to 1-THQ magnitude was highest within quasi equilibrium stages. Based on our product formation as illustrated here and above sections, overall reaction scheme for HDN of Quinaldine was proposed in Figure 7.

![Figure 7. Proposed reaction mechanism of Quinaldine (Q) HDN](image)

The coke formation over catalyst surface was analyzed in BELAB AB, Sweden, which is showed in Figure 8. The non-reactive catalyst contains small traces of coke after sulfidation, and cracking of solvent had reasonable amount of coke deposition which was studied through 360°C (can be observed from Table 1). Low temperature catalytic activity was more dependent on HYD, formation of 1-THQ was stronger and more stable in bonding with catalyst. High coke deposition (Figure 8) over 130 and 150°C defined the more Lewis acid active sites which consisting of sulfur vacancy on the Mo and Ni atom. Active sites with H atoms on the sulfur atoms (protons of SH⁻ groups) had not much influence to push over forward mechanism. In this regard, the alumina HDN results only HYD and metallic sites mainly influence in C-N cleave on ring-opening, results were compared in Table 2 and 3 with the different feed
HDN on alumina. Strongly stable 1-THQ binding over catalyst by both rings in lower thermal conditions [7, 15] required an high active catalyst or enough driving energy. During the forward reaction for complete HYD of both rings, reduction in coke formation for 240°C comparably as previous showed that DHQ have both ligand of bonding with transition metals. Even though, N-bonding was stronger than pi-bonding, which had strong binding in Lewis sites. Both aromatic ring in compounds relatively indicate of high coke deposition. Figure 6 shows similar bonding strength on adsorption concentration from quinaldine and intermediates (5-THQ) over catalytic site with excluded solvent occupants over surface.

Figure 8. Coke formation (carbon (% w/w)) in NiMo-1 spent catalyst for different temperature (To) (°C) on residence time 300 min using various feed like Q, 1THQ and 5THQ (lines show to guide eyes)

When C-N breaking initiate, pi-bond had the priority to bond over surface site, which mainly depends on its strength to withstand on catalyst. At 300°C, the rate of C-N cleavage was limited, but formed amine group escaped faster from sites by leaving rest of products as soon after C-N cleavage. Increase in active sites over C-N cleavage reduces the coke formation.

Increase in hydrogenolysis reaction might increase the vacancies in active sites due to fast escapes of products from active sites and also, neither inhibition of NH₃. In long residence time at 340°C conditions, the cracking slowly stood up with presences of traces of straight chain hydrocarbons. While, higher temperature, increase in solvent cracking and 5-THQ formation led to clogging of active sites which might reduce the catalytic efficiency. The steady increase in coke formation at 340 to 380°C was more influenced due to cracking of solvent as shown in higher reaction temperature of catalyst. Relative N-ligends on catalyst at higher temperature respectively reduced with dissociation in 1-THQ or DHQ with increases in rate of adsorption magnitude. However, formation of 1-THQ represented relatively low and increase in intermediate product concentration during formation and disappearances would keep sites busy with HYD and hydrogenolysis together. So, the impact of 1-THQ coking is lo at higher reaction temperature. Above 300°C, 5-THQ was gradually increased with benzene HYD, but it doesn’t impact on coke formation as noted in Figure 8. Slow C-N breakage rate had attend to lower detachment in pi-bonding of 5-THQ due to covalent nature of bonding. Thus the lower coke depositions through the 5-THQ path influence higher stability rather 1-THQ path for this investigated catalyst.
4. Conclusions

Below 210°C N-ring HYD was observed. Due to strong binding energy by Mo on N, might occupy by 1-THQ on active sites. Between 210 and 300°C, HYD showed formation in DHQ and traces of 5-THQ. Above 300°C, the reaction pathway consisted of Q, 1-THQ, DHQ, 5-THQ, BB and BCH. Unlike catalytic cracking, thermal cracking at C-N cleave induced BB formation. The path of 5-THQ ↔ DHQ reached equilibrium under lower partial pressure due to methyl group steric hindrance as studied under NiMo-1 and NiMo-2 catalyst. Hence, Q1 HDN results with approximately 6-fold lower concentration of 5-THQ than 5-THQ. Minimized steric hindrance on higher partial pressure favored higher rate of BCH formation. Therefore, 5-THQ and BCHE cannot be hydrogenated and should overcome barrier by H₂ pressure. The N-ring followed with benzene-ring HYD indicated the rate limiting step in this methyl-hindrance compound in Liquid-Phase HDN. Thus, weak pi-bond strength and low adsorption capability of 5-THQ limits the rate in benzene ring HYD and C-N cleavage. Also, inhibition of 1-THQ and 1-THQ in rapid dissipation of 5-THQ and 5-THQ from active site reduce the HDN conversion.

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