

New Catalyst for Biodiesel Formation: Synthesis, Structural Elucidation and Quantum Chemical Calculations of New Ni(II) Complexes

Sobhani, Shahin; Pordel, Mehdi⁺; Beyramabadi, Safar Ali*

Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, I.R. IRAN

ABSTRACT: *New Ni(II) complexes were synthesized from the coordination of the ligands derived from benzo[1,2-c]isoxazoles with Ni(II) cation.. The structure of the new complexes was characterized by elemental analyses, mass, and IR spectra. To gain a deeper insight into the geometry of Ni(II) complexes, a quantum chemical investigation was performed. The obtained results from experimental and theoretical arguments confirmed a square-planar geometry for Ni(II) complexes. These complexes were examined as homogeneous catalysts for the transesterification of corn oil with methanol. The structure of the obtained product was confirmed by ¹H NMR analysis. The catalytic results showed that the new Ni(II) complexes can be considered as potential candidates for the development of a new catalytic system for biodiesel production.*

KEYWORDS: *Benzo[1,2-c]isoxazole; Ni(II) complex; Catalyst; Biodiesel; Transesterification.*

INTRODUCTION

Demand for new energy sources that cause less pollution is constantly increasing in the world. Utilizing alternative fuels is one of the most feasible ways to meet this growing demand. Biodiesel is one of the most important of these fuels [1]. The main features of biodiesel fuel are high biodegradability, renewability, and low release of toxic and hazardous pollutants [2]. When triglycerides (vegetable or animal fats and oils) are being reacted with short-chain alcohols such methanol or ethanol by either acids or bases as a catalyst, biodiesel fuels are prepared. The advantages of the base-catalyzed reaction path include slower reaction times and lower catalyst cost than that acid catalyzes. However, high sensitivity to both water and free fatty acids is one of the weaknesses of alkaline catalysts. Also, the formation of soap as a byproduct is a problem in their use. Meanwhile, Lewis acids have significant properties such as the enhanced

stability, higher selectivity, easier handling, simple workup procedures, non-toxicity, non-corrosiveness, the mildness of the reaction conditions, ease of recovery, and reuse of the catalyst which has caused the use and development of new Lewis acid is increasing gradually.

Nickel-containing compounds play an important role in our daily lives such as food preparation equipment [3], mobile phones [4], medical equipment [5], transport [6], buildings [7], and power generation [8], etc. Moreover, Ni(II) complexes discover applications as a catalyst for many reactions such as the reduction of carbonyl compounds [9], ethylene polymerization [10], Suzuki–Miyaura cross-coupling [11], the electrocatalytic water oxidation [12], chemoselective alkene hydrosilylation [13], etc.

On the other hand, benzo[1,2-c]isoxazoles can be mentioned as one of the most important and widely used

* To whom correspondence should be addressed.

+ E-mail: mehdipordel58@mshdiau.ac.ir

1021-9986/2021/6/1757-1764 8/\$/5.08

heterocyclic compounds in various fields. They can be utilized as antipsychotic risperidone [14] and anti-HIV drugs [15] and play an important role in many organic reactions [16]. Isoxazole-metal complexes are also considered as intermediates in reactions of synthetic utility, for example, the reductive ring opening of isoxazoles [17].

Based on these aspects, herein, we have synthesized and characterized the new Ni(II) complexes. The quantum chemical investigation to gain a deeper insight into the geometry of Ni(II) complexes was also performed. In addition, these complexes were used as homogeneous catalysts for the transesterification of corn oil with methanol under different reaction conditions.

EXPERIMENTAL SECTION

Equipment and Materials

Melting points were determined in an Electrothermaltpe-9100 melting-point apparatus. Percentage of Ni(II) was measured by using a Hitachi 2-2000 atomic absorption spectrophotometer. The ^1H NMR (300 MHz) spectra were recorded on a Bruker Avance DRX-300 spectrometer. Chemical shifts are reported in ppm downfield from TMS as internal standard; coupling constant J is given in Hz. The FT-IR spectra were obtained as potassium bromide pellets using a Tensor 27 spectrometer and only noteworthy absorptions are listed. The mass spectrum was recorded on a Varian Mat, CH-7 at 70 eV. Elemental analysis was performed on a Thermo Finnigan Flash EA microanalyzer. Compounds **1** [18], **3** [19], **4** [20], **5** [21] and **7a,b** [22] were synthesized according to the published methods. Other commercially available reagents were used without further purification.

Computational methods

All of the calculations have been performed using the DFT method with the B3LYP functional [23] as implemented in the Gaussian 03 program package [24]. The 6-311++G(d,p) basis sets were employed except for the Ni atom where the LANL2DZ basis sets were used with considering its effective core potential. The geometry of the Ni complex was fully optimized, which was confirmed to have no imaginary frequency of the Hessian. Geometry optimization and frequency calculation simulate the properties in the gas/solution phases.

The fully-optimized geometries were confirmed to have no imaginary frequency of the Hessian. Also,

the calculations were done in both states of the Ni (II) complex, the high spin, and low spin.

The solute-solvent interactions have been investigated using one of the self-consistent reaction field methods, i.e., the sophisticated Polarizable Continuum Model (PCM) [25]. In both the gas phase and methanolic solution, the Zero-Point-Energy (ZPE) corrections were made to calculate energies.

General procedure for the synthesis of new complexes **8a,b** from compounds **7a,b**

Nickel (II) chlorohydrate hexahydrate (0.29 gr, 1 mmol) was added to the yellow solution of ligand **7a,b** (2 mmol) in aqueous methanolic solution (15 mL, MeOH, H₂O, 10:90). The reaction was carried out for another 1 h at rt. The complex was isolated by evaporation of the solvent and washed with cold MeOH and then H₂O.

[Ni(L1)₂]Cl₂ (**8a**): was obtained as a dark green powder. m.p. > 300 °C (decomp); yield: 87%. IR (KBr): 3442 cm⁻¹ (OH), 1637 cm⁻¹ (CH=N), ESI-MS (+) m/z (%): 928 [Ni(L1)₂]²⁺. Anal. Calcd for C₄₆H₃₂Cl₆NiN₈O₂ (1000.2): C, 55.24; H, 3.22; N, 11.20; Ni, 5.87. Found: C, 54.89; H, 3.19; N, 11.48; Ni, 6.05.

[Ni(L2)₂]Cl₂ (**8b**): was obtained as a dark green powder. mp > 300 °C (decomp); yield: 84%. IR (KBr): 3447 cm⁻¹ (OH), 1641 cm⁻¹ (CH=N), ESI-MS (+) m/z (%): 910 [Ni(L2)₂]²⁺. Anal. Calcd for C₄₈H₃₂Cl₄NiN₁₀O₂ (981.3): C, 58.75; H, 3.29; N, 14.27; Ni, 5.98. Found: C, 58.59; H, 3.27; N, 14.56; Ni, 6.13.

Transesterification

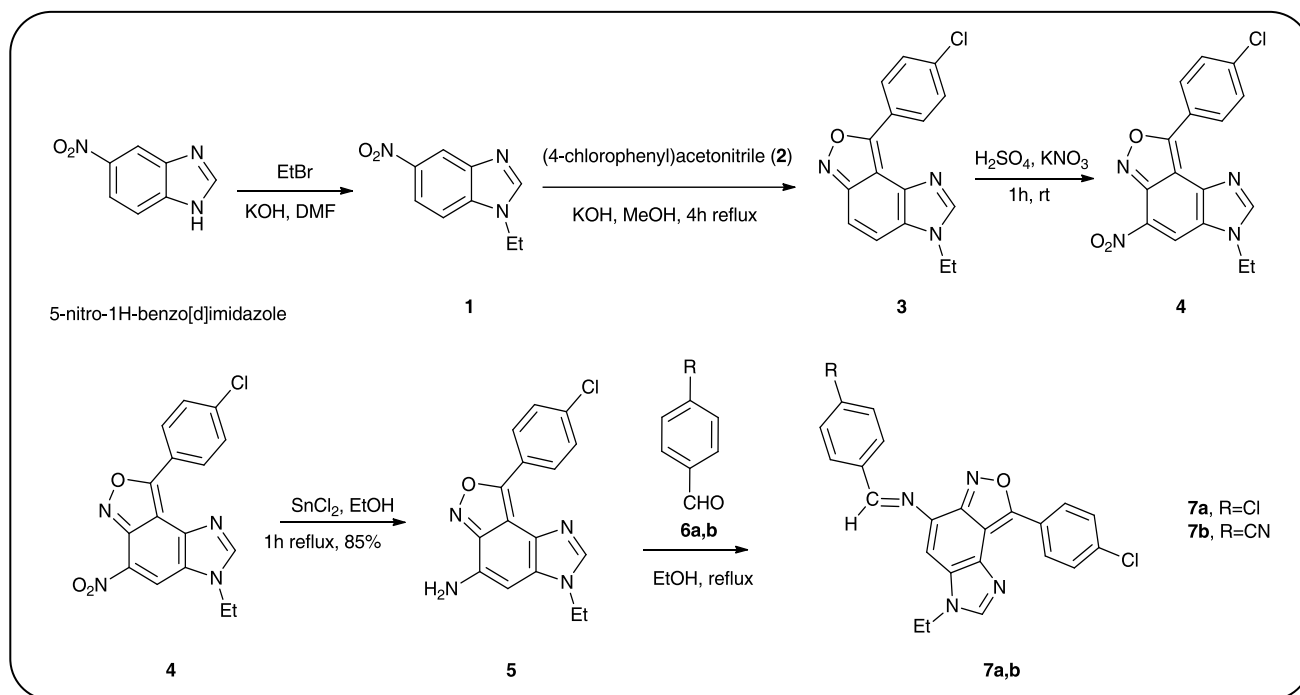
Ni(II) complex (**8a,b**) (2 Wt. %) was added as a catalyst to a mixture of methanol and corn oil (10:1). Transesterification reaction was performed under reflux condition at 25 h. The crude corn oil biodiesel phase was first separated *via a* separating funnel and then rotary evaporated. The yield of the Fatty Acid Methyl Esters (FAMES) formed was calculated by using Eq. (1).

$$\% \text{ Yield} = \frac{\text{Grams of methylester produced}}{\text{Grams of oil used for reaction}} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Synthesis and the structure of the new Ni(II) complexes **8a,b**

In the first step to obtain the new Ni (II) complexes, ligands **7a,b** were synthesized according to the following



Scheme 1. Synthesis steps of the ligand **7a,b**.

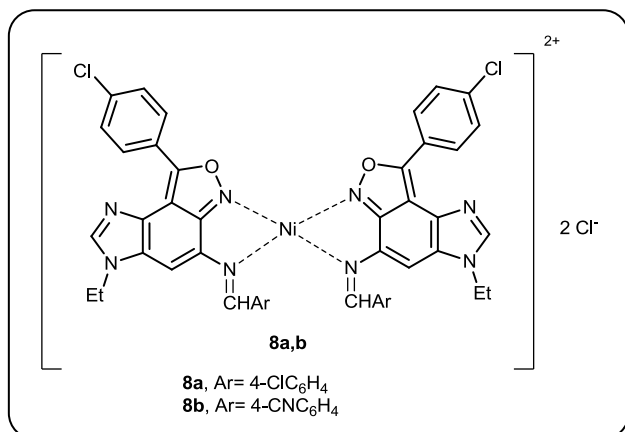
reactions (Scheme 1): 1-Ethyl-5-nitro-1*H*-benzimidazole (**1**) was obtained from alkylation of 5-nitro-1*H*-benzimidazole with ethyl bromide in basic DMF [18]. Then, 3-ethyl-8-(4-chlorophenyl)-3*H*-imidazo[4',5':3,4]benzo[1,2-*c*]isoxazole (**3**) was synthesized by reaction of compound **1** with (4-chlorophenyl)acetonitrile (**2**) in high yield [19]. The regioselective nitration of compound **3** using a mixture of sulfuric and potassium nitrate led to the formation of 3-ethyl-8-(4-chlorophenyl)-5-nitro-3*H*-imidazo[4',5':3,4]benzo[1,2-*c*]isoxazole (**4**) in good yield [20]. 3-Ethyl-8-(4-chlorophenyl)-3*H*-imidazo[4',5':3,4]benzo[1,2-*c*]isoxazol-5-amine (**5**) was obtained from the reduction of compound **4** in EtOH by SnCl₂ in good yield [21]. The reaction of compound **5** with aldehydes **6a,b** gave ligands **7a,b** in high yields [22] (Scheme 1).

Finally, new Ni(II) complexes **8a,b** were obtained from the reaction of ligands **7a,b** with Ni²⁺ ion in an aqueous methanolic solution. Percentages of the Ni(II), C, H, and N in complexes **8a,b** were measured by using an atomic absorption spectrophotometer and the elemental analysis data. The obtained results from the atomic absorption spectrophotometer and the elemental analysis plus the molecular ion peak at *m/z* 928 ([Ni(L1)₂]²⁺) and *m/z* 910 ([Ni(L2)₂]²⁺) strongly

proposed the [Ni(L)₂]Cl₂ formulae for the Ni (II) complexes **8a,b**.

To gain a deeper insight into the geometry of new Ni(II) complexes **8a,b**, DFT calculations at the B3LYP/6-311++G(d,p) level were used. Geometries of the ligands **7a,b**, and complex **8a,b** were optimized in both the gas phase and the PCM model, where the methanol was the used solvent. For example, Fig. 1 shows the optimized geometry of the complex **8a** with the labeling of its atoms.

As depicted in Scheme 2 and Figure 1, the ligand **7a** acts as a bidentate ligand, coordinates to the Ni (II) *via* the nitrogen atom of the amine group (–N=CH) and the nitrogen atom of the isoxazole ring. Except for the ethyl groups, the aromatic rings of the ligands are in the same plane. It leads to the greater overlapping of orbitals which is resulted to amplify the appearance of the signal in the visible region. Also, both of the ligands are in the same plane forming a square plane of the complex. The Ni-O and Ni-N bonds lengths and some of the calculated structural parameters of the Ni(II) complex **8a** are collected in Table 1. Based on our experimental results and theoretical arguments, a square-planar geometry was proposed for the new nickel complexes **8a,b** (Fig. 1).



Scheme 2: The structure of the Ni(II) complexes.

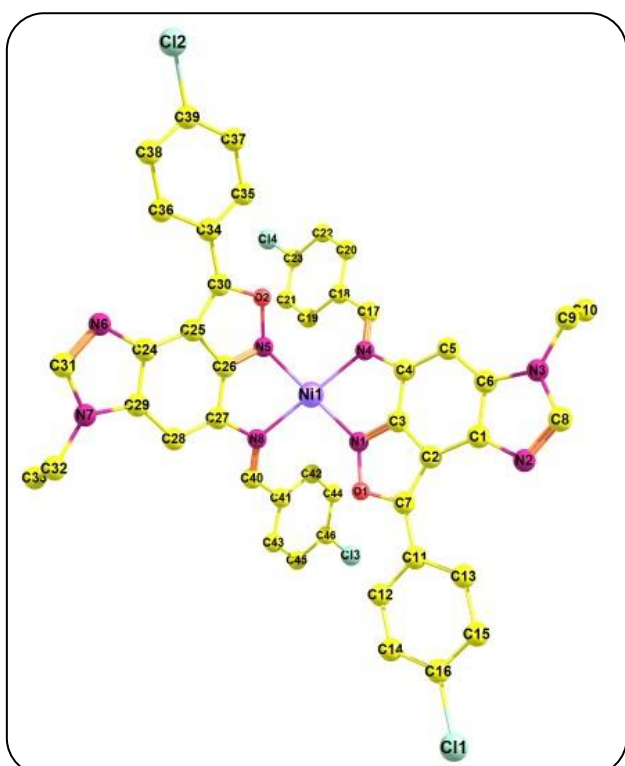


Fig. 1: The optimized geometry of the Ni(II) complex 8a.

Transesterification

Because new Ni(II) complexes (**8a,b**) have the Lewis acid character to activate the carbonyl groups in triglyceride moieties, they were used as homogeneous catalysts for the transesterification of corn oil with methanol. To explore the catalytic performance of Ni(II) complexes for transesterification, the methanolysis of corn oil to yield FAMES at reflux temperature, oil-methanol ratio (1:4, 1:6, 1:8, 1:10, 1:12, 1:14), catalyst dose (1 to 3%), and at different time intervals (1, 7, 14, 21, 25, 28h)

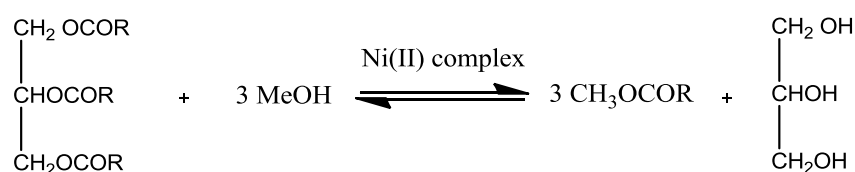
were performed. The criterion of optimized conditions was set to be the maximum yield obtained, which was calculated by using Eq. (1). Complex **8a** was used as a catalyst for optimization experiments. The results of % yield FAMES obtained are shown in Fig. 2. As can be seen in Fig. 2a, the optimal reaction time (25 h) was obtained under the oil-methanol ratio of 1:10 and 2.0 Wt.% of catalyst while keeping the reflux conditions, where the maximum yield achieved was 84%. Then, the oil-methanol ratio was increased using 2.0 Wt.% of catalyst and the same reaction time (25 h) at reflux conditions (Fig. 2b). As a result, the percentage yield of biodiesel was increased to the maximum of 84% under 1:10 oil-methanol ratio at 25 h reaction time. The increase in the biodiesel yield was possibly due to an excess amount of methanol which may refresh the catalyst surface by forming methoxy species and in turn shifted the reaction towards the forward direction. In the next step, under the optimized oil-methanol ratio of 1:10 and 25 h reaction time, catalyst dose was changed, where from Fig. 2c, it can be seen that maximum conversion of 84% was achieved with 2.0 Wt.% catalyst concentration. The observed increase in the percentage conversion with increasing catalyst concentration can be due to the availability of a more active site on the catalyst surface during the transesterification process. However, further increase in the catalyst concentration over 2.0 % might have resulted in the increase in viscosity of the system which in turn reduces the interaction between the catalyst and reaction medium [26].

Ni(II) Complex **8b** was also used as a catalyst for the reaction and the same results were obtained. The excess amount of methanol which may refresh the catalyst surface by forming methoxy species and in turn shift the reaction towards a forwarding direction [27] can lead to an increase in the biodiesel yield. Also, the availability of a more active site on the catalyst surface during the transesterification process can be proposed for the observed increase in the percentage conversion with increasing catalyst concentration.

The structure of the product was confirmed by ¹H NMR spectroscopy. The disappearance of the signals of methine protons in the range 4.12-4.23 ppm and observation of the signal at 3.43 ppm assignable to the methoxy protons established the conversion of corn oil into corn oil biodiesel. The percent conversion of corn oil into products calculated from Eq. (1) was 59-84 %.

Table 1: Selected structural parameters of Ni(II) complex 8a.

Bond	Bond length (Å)	Angle	(°)	Dihedral angle	(°)
Ni-O1	1.843	N1-Ni-N5	179.34	C28-N4-C42-C30	-121.280
Ni-N4	1.945	N4-Ni-N8	179.56	C26-C27-C29-C36	-38.348
Ni-N3	1.873	Ni-O2-N3	36.788	C2-C39-C40-C41	-179.327
Ni-N6	1.887	Ni-O1-C8	129.13	C37-C38-C39-C12	-179.043
Ni-N8	2.139	O1-C8-C6	119.76	N6-C22-C27-C29	-3.876
Ni-O2	2.228	Ni-N3-C1	113.66	N4-C25-C26-N5	1.068
N3-C1	1.512	C8-C15-C16	120.890	N5-C28-N4-C42	-177.781
O1-C8	1.204	C8-C6-C5	121.987	C26-C27-C36-C41	0.324
N6-C22	1.380	C29-C36-C37	121.651	O1-C8-C15-C20	22.540
C27-C29	1.450	O4-C29-C27	119.122	C15-C8-C6-C5	38.126
C27-C26	1.389	C27-C26-N5	129.603	C5-N2-C7-N1	-0.154
C25-C26	1.501	N4-C28-N5	114.650	N2-C5-C6-C1	-175.691
C36-C38	1.416	N4-C42-C30	113.870	C7-N1-C21-C9	-123.176
C25-N4	1.299	C42-C30-C35	120.346	C14-C9-C21-N1	56.783
C26-N5	1.354	C31-C30-C31	119.769	C10-C11-C12-C13	0.287



Scheme 3: General Transesterification reaction of triglyceride with methanol

Comparing the efficiency of the present method with the previous methods is shown in Table 2 along with the relevant references [28-31]. As can be seen, transesterification by alkaline catalyst (NaOH) shows relatively good results. But as mentioned in the introduction, one of the problems with using such catalysts is the formation of soap as a by-product. The results of using enzyme catalysts (entry 3) are almost the same as those of our catalysts. However, one of the problems with using enzymes is their relatively high cost. The other methods (entries 3 and 4), in addition to being less efficient than the proposed method, require a higher temperature to perform the reaction.

CONCLUSIONS

The reaction of ligands derived from benzo[1,2-

c]isoxazoles with Ni(II) cation led to the formation of new Ni(II) complexes in high yield. According to experimental results and theoretical calculation, a square-planar geometry was proposed for Ni(II) complexes. Ni(II) complexes were used as a new catalyst for biodiesel formation. New nickel (II) complexes can activate the carbonyl groups in triglyceride moieties and therefore they were used as homogeneous catalysts for the transesterification of corn oil with methanol. The results revealed that the new Ni(II) complexes can convert the corn oil into corn oil biodiesel and it has a high catalytic ability for biodiesel production. Comparing the efficiency of the present method with some previous methods showed that transesterification yield in the proposed method, is one of the most effective methods.

Table 2: Comparative the transesterification yield using the reported methods versus the present method.

Entry	Reagent and Conditions	Time (h)	Yield (%)	Ref.
1	Ni(II) complex 8a,b , reflux	25	84	-
2	NaOH, 50 °C	1	80	28
3	Lipase, 70 °C	24	83	29
4	Zeolites and ion-exchange resins, 150 °C	30	79	30
5	Biochar, 150 °C	3	48	31

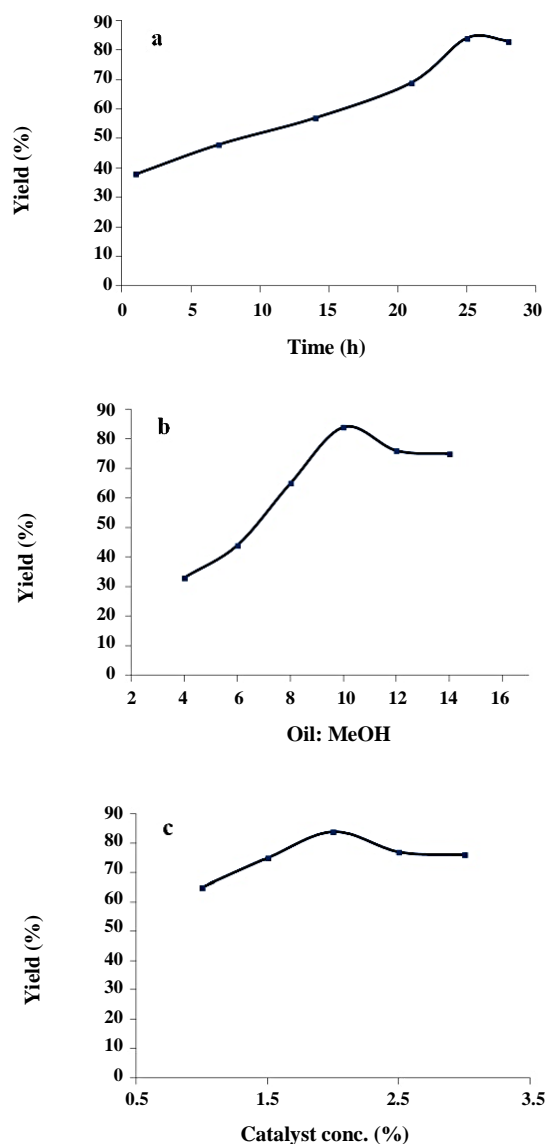


Fig. 2: Effect of various time intervals under the oil-methanol ratio of 1:10 and 2 Wt.% of catalyst (a), oil-methanol ratio using 2 Wt.% of catalyst and 25 h reaction time (b) and catalyst concentration under the optimized oil-methanol ratio of 1:10 and 25 h reaction time (c) on transesterification reaction.

Acknowledgment

We would like to express our sincere gratitude to the Research Office, Mashhad Branch, Islamic Azad University, Mashhad-Iran, for financial support of this work.

Received : May. 3, 2020 ; Accepted : Aug. 17, 2020

REFERENCES

- [1] Mahmudul H.M., Hagos F.Y., Mamat R., Adam A.A., Ishak W.F., Alenezi R., [Production, Characterization and Performance of Biodiesel as an Alternative Fuel in Diesel Engines—A Review](#), *Renewable and Sustainable Energy Reviews*, **72**: 497-509 (2017).
- [2] Aghbashlo M., Demirbas A., [Biodiesel: Hopes and Dreads](#), *Biofuel Research Journal*, **3(2)**: 379-379 (2016).
- [3] Gopinath S, Devan P. K. [Optimization and Prediction of Reaction Parameters of Plastic Pyrolysis Oil Production Using Taguchi Method](#), *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **39(2)**: 91-103 (2019).
- [4] Lande M.K., Magar R.R., Pawar G.T., Gadekar S.P., [Ce-ZSM-11 Zeolite: An Efficient Heterogeneous Catalyst for One Pot Synthesis of 4H-Pyran Derivatives](#), *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **39**: 91-104 (2018).
- [5] Soloveva A.Y., Eremenko N.K., Obratsova I.I., Eremenko A.N., Gubin S.P. [Synthesis and Optical Properties of Fe@ Au, Ni@ Au Bimetallic Core-Shell Nanoparticles](#), *Russ. J. Inorg. Chem.*, **63**: 444 (2018).
- [6] de Reuse H, [Inhibitors of HIV- 1 Protease by Using in Situ Click Chemistry](#) *Angewandte Chemie, International Edition, Int. J. Biol. Chem.*, 339 (2017)
- [7] De M., Bera S., Tewari H.S., [Self- Powered Cardiac Pacemaker Enabled by Flexible Single Crystalline PMN- PT Piezoelectric Energy Harvester](#) *Advanced Materials, Emerg Mater Res*, **1** (2017)

- [8] Hu X., Jood P., Ohta M., Kunii M., Nagase K., Nishiata H., Kanatzidis M.G., Yamamoto A., [Power Generation from Nanostructured PbTe-Based Thermoelectrics: Comprehensive Development from Materials to Modules](#), *Energ Environ Sci.*, **9**: 517 (2016).
- [9] Chakraborty S., Bhattacharya P., Dai H., Guan H., [Nickel and Iron Pincer Complexes as Catalysts for the Reduction of Carbonyl Compounds](#), *Accounts of Chemical Research*, **48(7)**:1995-2003 (2015).
- [10] Hu X., Dai S., Chen C., [Ethylene Polymerization by Salicylaldimine Nickel \(II\) Complexes Containing a Dibenzhydryl Moiety](#), *Dalton Transactions* **45(4)**: 1496-503 (2016)
- [11] Mastalir M., Stoßger B., Pittenauer E., Allmaier G., Kirchner K [Air-Stable Triazine-Based Ni \(II\) PNP Pincer Complexes as Catalysts for the Suzuki–Miyaura Cross-Coupling](#), *Organic Letters*, **18(13)**: 3186318-9 (2016).
- [12] Wang J.W., Hou C., Huang H.H., Liu W.J., Ke Z.F., Lu T.B., [Further Insight into the Electrocatalytic Water Oxidation by Macrocyclic Nickel \(II\) Complexes: The Influence of Steric Effect on Catalytic Activity](#), *Catalysis Science & Technology*, **7(23)**: 5585-5593 (2017).
- [13] Buslov I., Because J., Mazza S., Montandon- Clerc M., Hu X., [Chemoselective Alkene Hydrosilylation Catalyzed by Nickel Pincer Complexes](#), *Angewandte Chemie International Edition*, **54(48)**: 14523-14526 (2015).
- [14] Szarfman A., Tonning J., Levine J., Doraiswamy P., [Atypical Antipsychotics and Pituitary Tumors: A Pharmacovigilance Study Pharmacotherapy](#), *Pharmacotherapy*, **26**: 748-758 (2006)
- [15] Srirastara S., Bajpai L.K., Batra S., Bhaduri A.P., Maikhuri J.P., Gupta G., Dhar J.D., [Microwaves in Organic Synthesis](#), *Bioorg. J. Med. Chem.*, **7**: 2607 (1999).
- [16] Loudon J.D., Tennant G., [Substituent Interactions in Ortho-Substituted Nitrobenzenes](#), *Quart Rev.*, **18**: 389 (1964).
- [17] Munsey M.S., Natale N.R. [The Coordination Chemistry of Isoxazoles](#), *Coordination Chemistry Reviews*, **109(2)**:251-281 (1991)
- [18] Preston P.N., In [“The Chemistry of Heterocyclic Compounds, Benzimidazoles and Cogenetic Tricyclic Compounds](#), John Wiley & Sons, Part 1, Volume 40, pp 87–105
- [19] Rahimizadeh M., Pordel M., Bakavoli M., Bakhtiarpoor Z., Orafaie A., [Synthesis of Imidazo \[4, 5-a\] Acridones and Imidazo \[4, 5-a\] Acridines as Potential Antibacterial Agents](#), *Monatshefte für Chemie-Chemical Monthly*, **140(6)**: 633 (2009).
- [20] Ramezani S., Pordel M., Beyramabadi S., [Synthesis, Spectroscopic Characterization and DFT/TD-DFT Calculations of new Fluorescent Derivatives of Imidazo \[4', 5': 3, 4\] Benzo \[c\] Isoxazole](#), *Journal of Fluorescence*, **26(2)**: 513-519 (2016)
- [21] Agheli Z., Pordel M., Beyramabadi S.A., [New Fe \(III\) Complex with 8-\(4-chlorophenyl\)-3-butyl-3H-imidazo \[4', 5': 3, 4\] benzo \[1, 2-c\] isoxazol-5-amine \(5-AIBI\) ligand: Synthesis, Spectroscopic Characterization and DFT Calculations](#), *Journal of Molecular Structure*, **1130**: 55-61 (2017)
- [22] Sobhani S., Pordel M., Beyramabadi S.A., [Design, Synthesis, Spectral, Antibacterial Activities and Quantum Chemical Calculations of New Cu \(II\) Complexes of Heterocyclic Ligands](#), *Journal of Molecular Structure*, **1175**: 677-685 (2019)
- [23] Ou Q., Alguire E.C., Subotnik J.E., [Derivative Couplings Between Time-Dependent Density Functional Theory Excited States in the Random-Phase Approximation Based on Pseudo-Wavefunctions: Behavior Around Conical Intersections](#), *The Journal of Physical Chemistry B*, **119(24)**: 7150-7161 (2014).
- [24] Tomasi J., Mennucci B., Cammi R., [Quantum Mechanical Continuum Solvation Models](#), *Chemical Reviews*, 105(8):2999-3094 (2005).
- [25] Vosburgh W.C., Cooper G.R., [Complex Ions: I. The Identification of Complex Ions in Solution by Spectrophotometric Measurements](#), *Journal of the American Chemical Society*, **63(2)**: 437-442 (1941).
- [26] Teo S.H., Goto M., Taufiq-Yap Y.H., [Biodiesel Production from Jatropha Curcas L. oil with Ca and La Mixed Oxide Catalyst in Near Supercritical Methanol Conditions](#), *The Journal of Supercritical Fluids*, **104**: 243-250 (2015).
- [27] Teo S.H., Goto M., Taufiq-Yap Y.H. [Biodiesel Production From Jatropha Curcas L Oil with Ca and La Mixed Oxide Catalyst in Near Supercritical Methanol Conditions](#), *The Journal of Supercritical Fluids*, **104**: 243-250 (2015).

- [28] Gopinath S., Dineshbabu N., Bibin C., Murugan V.B., [Optimizing the Various Parameters for Biodiesel Production by Transesterification](#), *International Journal of Engineering Research & Technology*, **4(2)**: 716-718 (2015)
- [29] Bajaj A., Lohan P., Jha P.N., Mehrotra R., [Biodiesel Production Through Lipase Catalyzed Transesterification: An Overview](#), *Journal of Molecular Catalysis B: Enzymatic*, **62(1)**: 9-14 (2010).
- [30] Kiss A.A., Dimian A.C., Rothenberg G., [Solid Acid Catalysts for Biodiesel Production— Towards Sustainable Energy](#), *Advanced Synthesis & Catalysis*, **348(1- 2)**: 75-81 (2006)
- [31] Dehkhoda A.M., Ellis N., [Biochar-Based Catalyst for Simultaneous Reactions of Esterification and Transesterification](#), *Catalysis Today*, **207**: 86-92 (2013).