HYDROGENATION OF NITROBENZENE USING GLYCEROL WITHOUT MOLECULAR HYDROGEN

Er Abhi Soni[a,b], Er Saurabh Parmar[b,*], Er Niyati Makwana[b,*], Er. Kesha Naik[b,*]

Dr. Vaishali Umrigar[b,*]

[a]*Email Id : soni.abhi5655@gmail.com*

[b]*College : Sarvajanik College of Engineering Technology*

[*]*Corresponding Authors*

1. Abstract

The hydrogenation with UHPP (Ultra High Pressure Process) is a new technique in food cold sterilization which has broad application prospect. Other techniques for hydrogenation are with Super Critical Carbon Dioxide ($scCO_2$), with the use of green solvent like Glycerol, with the help of advanced technology Multimax for production of aniline from nitrobenzene. These are the few techniques for hydrogenation at industrial level. The ultra-high-pressure processing technique has already used and applied in production on a large scale. Most hydrogenation processes can be accomplished under fairly mild temperature; many important reactions require high pressure hydrogenation like example benzoic acid to cyclohexane carboxylic acid or in food industries over charcoal-supported transition metal catalysts in supercritical CO_2 medium for hydrogenation. In our reaction of hydrogenation the objective is to use catalyst or solvent as a hydrogen donor for the conversion of Nitrobenzene into Aniline without molecular H_2. In industry it requires harsh operating conditions to achieve the desired purity of the product. Hence as an intensified process, the experiments will be conducted to establish optimized conversion and selectivity of the products with varying the operating parameters like feed composition, solvent, catalyst (with or without) in proper dosage, temperature and reaction time. Also qualitative and quantitative analysis of the samples with GC/GCMS and relate them to the theoretical analysis of the reaction will be established which may be helpful at industrial level to scale up the process with detailed data analysis with the parameters like cost, quantity, quality, time, safety etc.

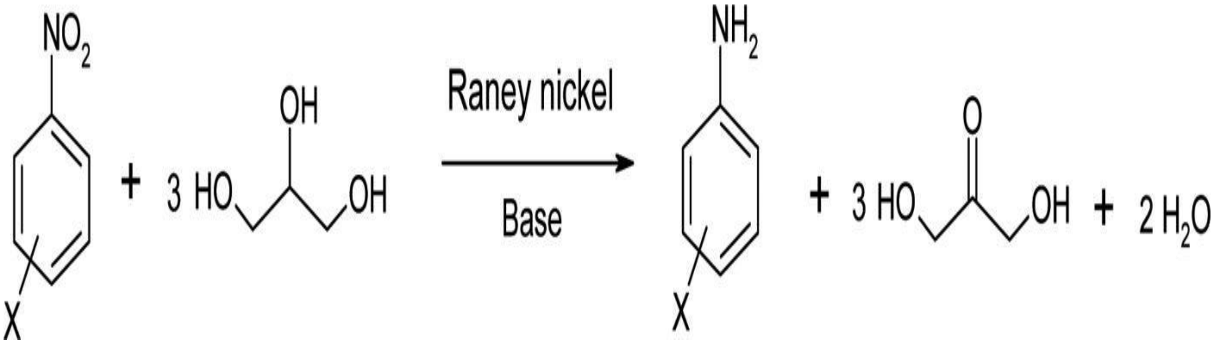
2. Keywords

Hydrogenation; Nitrobenzene; Glycerol; Gas Chromatography; Aniline

3. Introduction

Aniline and its derivatives are important building blocks in organic synthesis and are used in the synthesis of polyurethane, pharmaceuticals, and dyes, to name a few applications. Aromatic amines are usually produced via the catalytic hydrogenation of the corresponding nitro-aromatic compound with molecular hydrogen and different homogeneous and heterogeneous metal catalysts. Alternatively, transfer hydrogenation of aromatic nitro compounds using various organic molecules as hydrogen donors has also been reported. A key advantage of this alternate pathway is that it is performed in the absence of gaseous hydrogen, the presence of which requires extra precautions and special high-pressure equipment. In addition, for aromatic nitro-compounds bearing several functional groups, the catalytic transfer-hydrogenation reaction appears to be more selective than regular catalytic hydrogenation. Transfer hydrogenations are usually performed with the hydrogen donor in excess, and often that hydrogen donor also fulfills the role of solvent. The most commonly used hydrogen source is simple alcohols, especially, for example, 2-propanol. The transfer hydrogenation of nitrobenzene in 2-propanol is usually performed with various homogeneous and heterogeneous nickel and palladium catalysts using inorganic or organic base as the promoter.

In this study, glycerol was used as both solvent and hydrogen donor as it was dehydrogenated to dihydroxyacetone in the transfer hydrogenation of nitroaromatic derivatives and especially nitrobenzene, which was the representative aromatic nitro-compound. The catalyst was Raney nickel (RNi), and metal hydroxides were used as co catalysts. The effects on catalytic performance of reaction temperature, substrate concentration, and the loading of both catalyst and base were tested. In addition, catalyst recycling tests were also performed.



Transfer hydrogenation of nitrobenzene derivatives in glycerol.

In this report, the several reactions on the basis of hydrogenation are undertaking by different methods with in terms of changing catalyst, feed ratio, reaction time, temperature, pressure and methods of application. There are seven research papers described for different components and its particular catalysts.

- The authors Hongjun Wang and Fengyu Zhao are researched on hydrogenation with the help of super critical carbon dioxide ($scCO_2$) with different pressures of hydrogen and carbon dioxide and find its efficiency at particular pressure of it.

- The author Wu Han researched on the high pressure applications. He applies that high pressure on food cold sterilization and fined the quantity and quality on particular pressure.

- The author Alba E.Diaz-Alvarez and Victorio Cadierno researched on the hydrogenation with the help of glycerol which is green solvent. They used glycerol with different reactant with different catalyst and pressure and temperature. So they used glycerol used as a base for reaction.

- The author Kasibhatta J.Datta researched on the base free hydrogenation on the nitroarenes catalyzed by Micro-Mesoporous Iron Oxide with different reaction time and different solvents and find its yield and conversion with different reaction conditions.

- The author Prabhakar Bachu identified that iodine (I_2) is the best catalyzed transfer for hydrogenation and also he defined that it is low cost solvent and efficient solvent for particular reactant and base.

- The author Ananda S.Amarasekara and Muhammad A. Hasan researched on the conversion of levulinic acid to γ-valerolactone using alcohol as hydrogen donor under microwave conditions and used Pd/C as catalyst. In that reaction they used alcohol as a base for hydrogen.

- The author Dr. Fabio Visentin converts the nitrobenzene into aniline with the help of MultiMax instrument for better conversion which is high-tech technology for it.

- The author Yasutaka Kuwahara, Yasuhiro Magatani and Hiromi Yamashita also researched on the production of Gama velerolactone from the Levulinic acid and its esters. They did some reactions with ruthenium nanoparticles as a catalyst supported on Zr-containing mesoporous silica as a bifunctional catalyst.

- The author Majd Al-Naji et al, they suggest that Hydrogenation of levulinic acid (LA) towards Gama-valerolactone (GVL) is one of the most promising reactions in the field of biomass valorization to fine chemicals and liquid transportation fuels. Bimetallic Ni-Pt and Ni-Ru supported on ZrO2 and Gama-Al_2O_3 were successfully utilized in this work as highly active and GVL-selective catalysts for the solvent-free hydrogenation of levulinic acid (LA) using formic acid (FA) as a hydrogen source in a microwave reactor.

- Author Mohammad Ghith Al-Shaal et al they researched Microwave-assisted reduction of levulinic acid with alcohols producing Gama-valerolactone in the presence of Ru/C catalyst.

So we review some papers which are based on hydrogenation, catalytic hydrogenation, and high pressure and also refer papers in which hydrogenation of same component but different catalyst. This research papers are helpful for the experiment analysis of nitrobenzene with glycerol using different catalyst. The experimental analysis and results for particular research paper and also our experiment are discussed. We did 2 experiments with different catalyst.

4. Experimental

In first stage practical, we take 50 ml of Nitrobenzene and 150 ml glycerol. This liquid mixture is treated with Sulphuric acid and hydrochloric acid at temperature 60°C. At this temp we also add the titanium dioxide as a catalyst for the reaction. After this heating and mixing step then we have to separate out this mixture so we do simple distillation of liquids. In distillation we maintain the temperature 84°C. Because the boiling point of ammonia is 84°C. We separate out the aniline from liquid mixture. So based on some research papers we try this reaction with titanium dioxide and with Tin dioxide and also we will do this experiment with the help of iron oxide.

In second stage of this reaction, we try three different parameters for more accurate results. For this 3 experimental setup are installed. In first, second and third setup we take 34.18, 40, 50 ml nitrobenzene and 24.36, 20, 20 ml glycerol respectively. This taken amount based on ration of (N.B/glycerol). The heating temperatures for reaction are 80,100,120°C respectively. The catalyst for this reaction is AFS (Ammonium Ferrous Sulphate).

After first part of second stage, the separation of aniline from nitrobenzene and glycerol mixture is carried out by distillation setup. Three distillation setup installed at one time. After distillation volume of aniline is taken out and purity of aniline is measured by GC procedure.

Table:- experimental setup for second stage

Setup	**Nitro benzene(ml)**	**Glycerol(ml)**	**Temperature**	**After heating total quantity(ml)**	**Aniline quantity(ml)**
1	34.18	24.36	80°C	50	27
2	40	20	100°C	53	25
3	50	20	120°C	60	37

This above table shows entire experimental procedure and quantities of reactant and product.

Experimental setup of hydrogenation reaction

Experimental setup of distillation

On the basis of research paper there are comparisons of their reactions for different reactants with different time, temperature, catalyst, pressure.

Author	**Types**	**Compounds**	**Catalyst**	**Temp**	**Pressure**	**Time**	**Reference No.**
Hongjun Wang	$scCO_2$	Benzoic acid	Rh/C	80°C	H2:10Mpa CO2:10Mpa	--------	2
Wu Han	UHPP	Fruit Juice	Enzymes	60°C	600 MPa	30 min	3
Alba E.Diaz-Alvarez	Glycerol	Carbonyl	KOH	80°C	----------	2 – 2.5 hr	4
	Glycerol	Oleic acid	NiO/Al2O3	250-270°C	----------	3 hr	

	Glycerol	Nitroarenes	Fe3O4-Ni +KOH	400°C	----------	24 hr	
	Glycerol	Other organic molecules	Silica AI-SBA-15	150°C	----------	3 hr	
Kasibhatta J.Datta	Iron oxides	Nitroarenes	Micro-meseporous Iron Oxides	70°C	---------	40 min	5
Prabhakar Bachu	I_2	Aldimines, Ketimines, amino	I_2	25°C	---------	---------	6
Ananda S.Amarasekara	Pd/C	Levulinic acid	Pd/C	90°C	---------	3 hr	7
Yasutaka Kuwahara	RN	Levulinic acid's ester	RN	70°C	0.5 MPa H_2	---------	8
Mohammad Ghith Al-Shaal	Alcohol as base	Levulinic acid	Ru/C	160°C	---------	25 min	9

(Table 1: it show the simple reaction procedure with catalyst, time, pressure, temperature of ten authors researches)

5. Result and Discussion

In first stage experiment, after the distillation and separation we do the confirmative taste of aniline. We find out the positive response of aniline. For quality analysis we do the GC(Gas Chromatography). With the help of GC we get nearly 40.23% pure aniline. So this purity can increase with increasing heating capacity, azeotropic distillation or steam distillation, with industrial equipment.

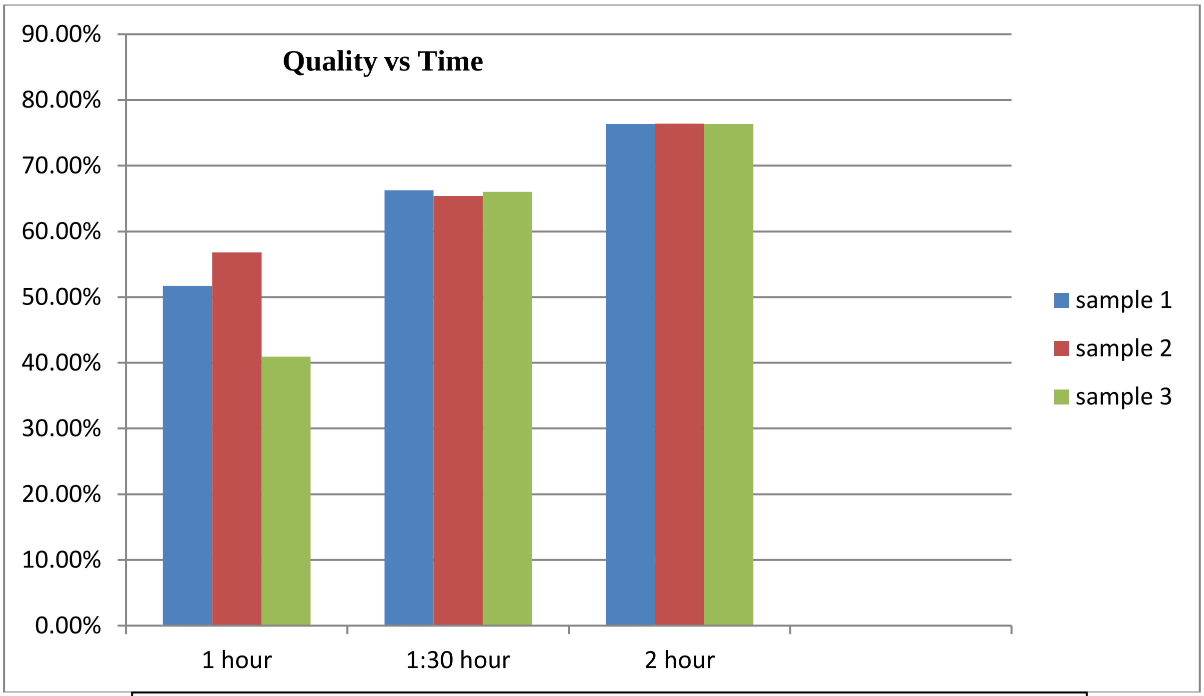
Catalyst	Reactant-Base	Quantity taken	Reaction	Temp.	Time	Product quantity	Product quality
TiO_2	Nitrobenzene-Glycerol	50 ml-150 ml	Hydrogenation	60°C	1-1.5hr	35 ml	40.23%

In second stage experiment, after heating and distillation procedure the confirmative test is carried out and achieve positive results and for purity GC is use. The results of GC are shown below in the table and also the retention graph.

Setup	Purity of aniline
1	51.68%
2	56.82%
3	40.92%

This table shows the aniline production is possible with the help of glycerol by changing temperature and quantity ratio and if we change in time for heating reaction the better results we can get. For time variation by theoretical table is plotted.

Setup	**Time**	**Quality**
1	1:30hr	66.25%
2	1:30hr	65.4%
3	1:30hr	66%
1	2hr	76.32%
2	2hr	76.4%
3	2hr	76.36%



Graph of quality with respect to time variation of sample 1, 2, 3

This results shows our experiments by changing feed parameters like concentration ratio of reactant, heating temperature and time variation for heating.

By changing concentration ratio we can observe that at ratio of 2 the reactants highly react with each other and give maximum product.

By changing heating temperature we can observe that at 100^{o}C the product quality of aniline is higher than 80^{o}C and 120^{o}C.

By changing time variation we can observe that if heating time increase than reactants more react with each other and gives high quantity and quality.

In this reaction, Ammonium ferrous sulphate ($(NH_4)_2SO_4*FeSO_4*6H_2O$) is used as catalyst and one question is arise for this reaction is that Is AFS is used as catalyst or reactant? For check this, electromotive force is necessary to determine for catalyst [1].

In Ammonium ferrous sulphate, ions are NH_4^+, SO_4^{2-}, Fe^+, SO_4^-, O_2^-, H^+ The hydrogenation of these ions or electron acceptances is calculated by EMF.

For NH^{4+} :-
EMF= -3.04V

For SO_4^{2-} :-
$SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O$
EMF= 0.17V

For Fe^+ :-
$Fe^+ + e^- \rightarrow Fe$
EMF=0.77V

For SO4- :-
EMF=0.085V

For H^+ :-
EMF=0.0V

For O^{2-} :-
EMF=1.23V

Now summation of EMF to check,
= -3.04+0.17+0.769+0.083+1.23
= -0.788V

Here the EMF is in negative, therefore the note is “if cell potential is negative the reaction will not occur until apply a voltage greater than cell potential.” By this note, catalyst which we used for hydrogenation is not suitable. Therefore answer of the question is AFS is not useful as catalyst or reactant in this reaction.

Final 3 samples of aniline

6. Conclusion

In conclusion, based on these six researches with different reactants with different parameters and our experiment, it conclude that based on the reactants which we want to hydrogenation the parameters are chosen like catalyst, pressure and temperature. Green solvents are more preferable because it is less expensive and easily available like glycerol and iodine (I_2). But there is limitation is that green solvent is not reacting with all reactant or in room conditions. Based on second stage experiment by changing feed parameters we get best results and also the heating time variation effect the reaction. The latest technologies like multimax, $scCO_2$ and UHPP are used at high cost for fast reaction, quality and quantity basis. There is using base for some reaction is preferable but for some reaction base free is suitable. The concept of levulinic acid to the Gama-valerolactone is also useful because of its high selectivity, efficiency and also with base or without base technique.

7. Future scope

In future, the application of UHPP, $scCO_2$ and multimax will widely used but there are more cost is there and major engineering problems are there. If reactor or boiler is blast due to high pressure there will be lost of production and lots of life may be. Environmental disaster is there if hazardous reactant is used. Therefore more restriction must be there and usage of green solvent has to increase for better environment protection. Industries have to use green solvent for reaction because green chemistry is more reliable. So there are both possibilities here either chooses green solvent or particular catalyst.

8. References

1. www.vaxasoftware.com/doc_eduen/qui/tpotred.
2. Alba E.Diaz-Alvarez, Victorio Cadierno.(2013). Glycerol: A promising green solvent and reducing agent for metal-catalyzed transfer hydrogenation reactions and nanoparticles formation. *Appl. Sci*.
3. Ananda S.Amarasekara, Muhammad A. Hasan.(2015). Pd/C catalyzed conversion of levulinic acid to γ-valerolactone using alcohol as a hydrogen donor under microwave conditions. Department of Chemistry, Prairie View A&M University.
4. Dr. Fabio Visentin et al.(2007). Hydrogenation of nitrobenzene to aniline. Metter-Toledo AG. *AutoChem*.
5. Hongjun Wang, Fengyu Zhao(2007). Catalytic ring hydrogenation of benzoic acid with supported transition metal catalyst in $scCO_2$. *Int. J. Mol. Sci.*
6. Kasibhatta J.Datta et al.(2016). Base-free transfer hydrogenation of nitroarenes catalyzed by micro-mesoporous iron-oxide. *Article in ChemCatChem*.
7. Prabhakar Bachu et al., Molecular iodine catalyzed transfer hydrogenation: Reduction of aldimines, ketimines, and α-imino esters. Department of Chemistry, Gakushuin University, Tokyo, Japan.
8. Wu Han et al.(2010). Research development of ultra-high pressure processing on fruit juice. Chinese Academy of Agriculture Mechanization Sciences, Beijing, china.

9. Yasutaka Kuwahara et al.(2015). Ru nanoparticles confined in Zr-containing spherical mesoporoussilica containers for hydrogenation of levulinic acid and its esters into Gama-valerolactone at ambient conditions. *Catalysis Today 258 (2015) 262–269*, Japan.
10. Majd Al-Naji et al.(2016). Insights into the selective hydrogenation of levulinic acid to Gama-valarolactone using supported mono and bimetallic catalysts. *Journal of Molecular Catalysis A: Chemical 417 (2016) 145–152*, spain.
11. Mohammad Ghith Al-Shaal et al (2016). Microwave-assisted reduction of levulinic acid with alcohols producing Gama-valerolactone in the presence of Ru/C catalyst. *Catalysis Communications 75 (2016) 65–68*, Germany.