

Chemical Waste Treatment Of Liquefied Gas Containers Using Sustainable Green Nanomaterial

Wafaa Mekheel Hasan , Hussein A.H. Al-Keriawy and Alaa K.H. Al-Khalaf*

Department of Environment Pollution, College of Environmental Sciences, Al-Qasim Green University, Al-Qasim District 8, Postcode 51013, Babylon province, Iraq.

Abstract

The present study dealt with the problem of waste formation which is a mixture of liquid, solid and gas materials in the liquefied gas containers through their maintenance process at the gas-fuel station. The waste from the cooking gas containers was analyzed using a Gas-Mass Chromatography (GC-MS) and an Infrared Spectrophotometer-Fourier Transform (FT-IR) to find out their components and then treat them using solid catalyst of calcined nano bentonite clay over reaction time (24 and 48 hours) with convenient stirring. The calcined nano bentonite clay has a high oxidative-catalytic ability to break down hydrocarbons into shorter chains due to the possession interchangeable protons distributed through clay surface and that led to new production of dominant hydrocarbon with longer chains such as (2-Furanol, tetrahydro-2,3-dimethyl-, trans) that amounted to (74.09[']/.) of the total summit area, due to its high surface area, high dispersion, and converting all produced hexane (49.35%) over reaction time (24 hours). The results showed that the use of solid catalysts had a clear role in treating these wastes cleanly and converting them into other chemical forms that could be used if they were exploited industrially.

Keywords: Chemical waste, Green Chemistry, Nanomaterials, Nano bentonite Clay

Introduction

The concern for environmental preservation and sustainable development of human activities is a topic of great importance. Society's great desire for sustainability requires organizations (especially those that pollute the environment or have the potential to pollute the environment) for a more harmonious coexistence and a balanced environmental development of their activities. (Abdullayev et al,2011; Albanis et al,2000; Ali and Khan,2017). The efforts to improve pollution levels, both related to air, water, soil and other environmental parts are especially necessary due to the growing interest in combining economic development with sustainability. Environmental pollution is one of the major challenges in modern human society (Al-Khalaf, 2015; Ankerfors, 2012) With urbanization and the rapid increase in the number of vehicles of various types in most countries, there has been an increase in air pollution. Several epidemiological studies have documented a decrease in lung function associated with long-term exposure to polluted air. (Anyakora, 2007; Aon ort al2000; Aprajita and Sharma, 2011).

Gas stations represent an important source of soil and water pollution, (FREIRE et al 2014) where the environment in which the gas stations are constructed exposes workers in the stations to many health risks and damages, which should be considered harmful to those workers. Among the dangers are contact with fuel and other chemical products, being near pumps, noise, etc. (ROCHA, et al. 2014) Volatile organic compounds pose

severe health risks from inhalation such as headache, asthma, fatigue, throat and eye irritation, nausea and even risk of explosion.(EMARAet al. 2010; PEREZ-RIAL, et al. 2009; TERRÉS, et al 2010)

Hydrocarbon fuels (gas, liquid, and solid) are the combustible or energy-generating types that can be harnessed to generate mechanical energy. Most of the widely used liquid fuels are derived from fossil fuels. Pollution with petroleum hydrocarbons is a harmful aspect of environmental pollution that negatively affects public health. Hence, it is essential to determine the levels of hydrocarbons in the environment. Petroleum hydrocarbons are a class of diverse organic compounds that contain two or more aromatic rings molten carbon and hydrogen atoms. They are ubiquitous environmental pollutants. At ambient temperatures, hydrocarbons are colorless or yellowish solids. (Anyakora, 2007)

Common general characteristics of the class are its high melting and boiling point, low vapor pressure, low solubility in water, and high solubility in fats, its water solubility tends to decrease with increasing molecular mass. The volatile hydrocarbons are highly lipid soluble and are absorbed from the lung, intestine and skin, in addition to being higher in humans who live in urban and industrial areas than in the outer suburbs.(Larsen and Larsen 1998).

The mixture of propane (C_3H_8) and butane (C_4H_{10}) gas, known as liquid gas. It was not used in homes until 1958, when it was produced as a by-product in Dora refinery, bottled in gas bottles commonly used today.(EMARA, et al. (2010)

Liquefied petroleum gas produced during petroleum refining can contain olefins, especially propylene and butylene (butene), which is produced from the refining process. These olefins are sometimes separated and used as intermediate materials for other processes.(Gary et al,2007)

Liquefied petroleum gas (LPG) or cooking gas is a clean combustion and effective cooking fuel used by nearly three billion people. It has long been considered an ambitious fuel option for many of the urban and rural poor. Some of the surplus is vented or burned at the site's oil and gas production, wasting this valuable fuel resource and releasing carbon back into the atmosphere.(Grieshop et al,2011)

In general, LPG can be distinguished from other energy sources on the basis that it combines portability, convenience, high energy, low sulfur content and clean combustion nature. LPG is colorless and odorless. The characteristic odor is an additive to help detect leaks and it is usually Thiophene. Unlike natural gas, LPG can easily be liquefied under moderate pressure.(Bizzo et al,2011)

Nanotechnology can be mentioned as the development, synthesis, characterization and application of materials and devices by modifying their size and shape at the Nano scale. It is a mixture of physics, chemistry, materials science, solid state, and biological sciences. So deep knowledge in one area will not be sufficient, and joint knowledge of physics, chemistry, and materials science, solid state and biological sciences is required. Nanotechnology applications are spread across nearly all branches of science and technology. The difference between Nano science and nanotechnology is that Nano science gives knowledge about the arrangement of atoms and their basic properties at the Nano scale level while nanotechnology is the technology used in command management at the atomic level to synthesize new nanomaterials with different properties.(Kolahalam et al2018)

They are minerals that are available with a large variety of physical and chemical shapes and properties. Several reviews describe their structure and characteristics in addition to their application in stimulation, drugs, tissue engineering, and as fillers for bio-compounds. From a chemical point of view, the clay is made of hydrated aluminum silicates, with a variable level of other elements such as magnesium, iron, calcium and potassium. Clay usually has a grainy side and becomes plastic when mixed with water, or solid when burned. Recently, the development of nanotechnologies and the perspective on their use in cultural

heritage preservation has led to an emphasis on clay minerals as raw materials for building advanced nanostructures. In the last decade of the twentieth century, modern nanotechnology has focused on carbon nanotubes and carbon nano fibers due to their excellent properties as a filler for many materials that enable a large number of applications.(Joussein et al ,2005).

The actual development of carbon-based nanostructures in cultural heritage applications is represented by the high cost, some respiratory risks, and pollution due to toxic solvents, as well as environmental concerns related to the accumulation of insoluble residues from synthetic carbon-based nanomaterials. Thus, natural materials, such as natural clays with a wide range of shapes at the Nano scale, are attracting increased attention. In pharmaceutical technology, natural source vectors were already well positioned versus synthetic materials. (Ruiz-Hitzky et al, 2010; Viseras et al, 2010)

Calcination is the process of removing impurities from zeolite and clay by heating 550 ° C for six hours in air. This process leads to the formation of a Lewis acid with depending on aluminum which works by obtaining an electron pair instead of the Bronsted acid sites by removing the hydroxyl group from the water. Calcination process may destroy the clay sheets; thus, the surface area will increase, and irregular grooves and cavities may form.

However, both Bronsted and Lewis acid sites are presented in zeolite and clay structures, depending on temperature. As a result, several acid centers can be formed which act as electron paired receptors, as the following figure (1).(Al-Khalaf et al.2012 ; Smith et al.2012 ; Al-Khalaf2015)

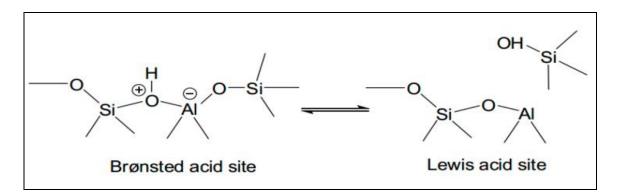


Figure (1) the solid catalyst of Lewis and Bronsted acid

It is becoming increasingly imperative to demand products made from renewable and sustainable resources that are biodegradable, non-petroleum-based and have low risks to the environment and human health. (Turbak et al,1983 ; Hubbe et al,2018 ; Siró and Plackett, 2010).

In this paper, the principles of green chemistry have been applied in the treatment of household cooking gas containers' waste by using nano bentonite clay to convert it into a clean production of long-chain hydrocarbon derivatives that are expected to be useful in the petrochemical industry.

Materials and method:

1. Materials

In this research, the principles of green chemistry and sustainable development were relied upon with the aim of preserving humans and the environment by using chemical pollution treatment techniques. So, it has been

used the calcined nano bentonite clay by mixing with waste and hexane as a solvent over homogenous stirring for the reaction time.

2. Waste treatment

Add (0.2g) of calcined nano bentonite clay to (0.2g) of waste of gas container in a glass flask of (50 ml) to be then dissolved in (25 ml) of hexane solvent, with a reaction time of (24, 48) hours with continuous stirring by means of an electromagnetic stirrer. After that, the reaction mixture was filtered under vacuum pressure, where the slurry was washed with hexane and acetone solvent at a rate of (5) milliliters each, after which a sample was taken from the resulting filtrate mixture for the purpose of analysis with a gas chromatographymass spectrometry (GC-MS) device.

Results and discussion:

1. FT-IR Analysis:

Results of the analysis of waste using an infrared spectrometer-Fourier transform, that there are three clear peaks after the fingerprint region, which extends from (500-1500 cm⁻¹) and it is a peak at a wavelength number (1649 cm⁻¹), the boundaries in which a band is present (C=C). The second peak appeared at a wave number (2924 cm⁻¹), which is the boundary that includes the (C-H) splicer of the type of SP³ hybridization. The third peak appeared at a wave number (3365 cm⁻¹), which represents region of the following atoms bonds (N, H, O), and according to the wave number and the shape of the crest, we deduced that it is belong to the (N-H) and (O-H) bonds as it is clear from figure (2). (Harthcock, and Atkin, 1988 ; Choo et al,1996).

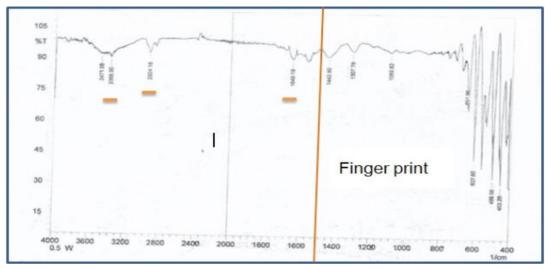


Figure 2: FT-IR analysis of gas container waste

2. GC-MS Analysis

The household gas container waste sample was analyzed before the treatment by (GC-MS) technology and the main components were identified by the emergence of seven high peaks mainly, as the highest percentage of the area belonged to the compound cyclohexane, as in Table (1).

Table (1) GC-MS analysis of waste before treatment

Table (1) GC-MS analysis of waste before treatment

NO.	Name of compound	Formula	Peak Area%	
1	n-hexane	C ₆ H ₁₄	6.54 %	
2	Hexane,3,4-dimethyle	C ₈ H ₁₈	9.86 %	
3	1-Pentene,2-methyl	C ₆ H ₁₂	12.77 %	
4	Cyclohexane	C ₆ H ₁₂	16.42 %	
5	Pentane,2,3-dimethyle	C ₇ H ₁₆	7.08 %	
6	Sulphuric acid dibutyl ester	$C_8H_{18}O_4S$	7.06 %	
7	Cyclohexylmethyl s-2-(dimethyl amino) ethyl	$C_{14}H_{30}NO_2PS$	6.51 %	
	propylphosphonothiolate			

From the above table, many derivatives of organic sulfur and phosphorous elements appear as hydrocarbon pollutants.

When the waste has been treated by using an equivalent amount of calcined nano bentonite over reaction times (24 and 48 hours) the productivity occurred and increased in both treatments, with different percentages between them as the GC-MS analysis data from the following table (2).

The reaction technique depends on the catalytic activity over time function kinetically, and the productivity percentage increased with new compounds to reach over (92.54%) when increasing the reaction time from 24 into 48 hours. Due to their high surface area, high acidic sites, high contents of exchangeable protons, high reactivity, and absorbency. However, calcined nano bentonite clay particles play an important role in removing hydrocarbons by recycling and converting them to another new compounds.

Table (2) GC-MS	analysis	after	treatment	by	using	calcined	nano	bentonite	clay	48-hour	reaction
24-hour reaction											

NO.	Name of	Formula	Peak	NO.	Name of compound	Formula	Peak
	compound		Area%				Area%
1	n-hexane	C_6H_{14}	49.35	1	heptane, 4-methyl	C ₈ H ₁₈	0.81%
			%				
2	pentane, 2-	C_6H_{14}	4.75%	2	2-furanol, tetrahydro-2,3-	$C_6H_{12}O_2$	74.09
	methyl				dimethyl, trans		%
3	octane, 4-methyl	C ₉ H ₂₀	4.44%	3	1-methoxy-2-propyl acetate	$C_6H_{12}O_3$	24.58
							%
4	2,4,6,8-	$C_{15}H_{30}$	3.60%	4	3-hexene-2,5-diol	$C_6H_{12}O_2$	0.03%
	tetramethyl-1-						
	undecene						
5	oxalic acid, hexyl	$C_{11}H_{20}O_4$	2.19%	5	Cyclopropane, 2-methylene-1-	$C_{12}H_{24}Si$	0.05%
	propyl ester				pentyl-1-trimethylsilyl		
6	2,2-	$C_7H_{14}O_2$	1.43%	6	2-	$C_{23}H_{50}O_5Si_3$	0.08%
	dimethylvaleric				[(trimethylsilyl)oxy]tetradecanoi		
	acid				c acid, bis(trimethylsilyl) ester		
7	sulfurous acid,	$C_9H_{20}O_3S$	25.40	7	4-chloro-3-n-	$C_9H_{17}CIO$	0.05%
	isobutyl 2-pentyl		%		butyltetrahydropyran		

	ester						
--	-------	--	--	--	--	--	--

From the above table, through reaction time of one day (24 hrs), the amount of hexane production increased to around (50 %) of the total according to the peak area, with the remaining (25%) of the organic acidic sulfuric derivative, which could be the reason for the presence of sulfur from thiophene additives.

On the other hand, with a longer reaction time (48 hrs), furanol derivative was obtained with a high production of (74.09 %) according to the peak area, with the remaining of propyl acetate derivative appearing at (24 %) of the total production, along with the presence of organic derivatives of acidic silicon in small percentages compared to the main peaks.

This is caused by the nature of the calcined nano-calcined bentonite over collapsed sheets of silica with high ability to dispersion and cracking chains of hydrocarbons by oxidation-catalytic process, then collecting them together according to their kinetic stability, type of interaction, and nature of organic linkage among each building units of new formation of hydrocarbons.

According to what was demonstrated in the previous studies, hydrocarbon pollutants are considered a dangerous environmental problem that affects all different environments (water, air, soil), and thus on humans.

However, the problem of removing any pollutant requires great efforts and advanced green processing techniques that are recyclable and inexpensive. Recently, many researchers tend to develop new high-quality materials with the help of some materials of natural origin, which have certain physical and chemical properties, that make them play a large and important role in the treatment process in a highly efficient and clean manner.(Prabhu, and Prabhu 2018).

It was previously thought that the role of clay in removing pollutants results from two possibilities of interaction between the clay particles and the pollutants. Either the clay particles absorb or adsorb the pollutants. In recent times after the emergence of related studies, it was clear that the use of solid acid catalysts in pollutant treatment processes, the mechanism of its action following the steps of catalytic treatment caused by the acid sites on the surface and pores. The exchangeable proton is sufficient to cause oxidation and cracking of pollutants. Therefore, nanoparticles reduce the concentration of pollutants and thus their harmful effect on the environment. (Nowack and Bucheli, 2007). George et al, 2018; Lvov et al, 2016)

The current study shows that the use of catalyst works to solve the problem through a catalyticoxidative reaction, where the results of the treatment process, which was for a period of times (24 and 48 hours) and with the use of calcined nano bentonite clay were shown at a ratio of (0.2g) with the same amount of waste, it was effective in the process of treating the waste, and converting it into other compounds with longer carbon chains.

Conclusions:

Through the results of the practical study on treating chemical pollution with sustainable green nanomaterial, the following significant points were reached:

1. Green treatment method by using catalyst of calcined nano bentonite clay showed great agreement on its effectiveness in treating chemical contamination with ease of application of reaction conditions and without any effect, addition, modification or special conditions, and no chemical change in the chemical composition of the solid catalyst.

2. Calcined nano bentonite clay showed a high catalytic ability to break down hydrocarbons from waste into shorter chains due to the possession of protons interchangeable through clay surface at acidic sites, layers and folds, and the production of new dominant hydrocarbons with longer chains such as (2-Furanol, tetrahydro-2,3-dimethyl-, trans) that amounted to (74.09¹/.) of the total summit area, due to its high surface area.

3. The results of (GC-MS) showed that breaking down the waste in a longer reaction time (48 hours) gave clear results that were better than the reaction with a period of (24) hours by converting all produced hexane.

Conflicts of Interest:

The authors declare no conflict of interest.

References

- Abdullayev, E., Sakakibara, K., Okamoto, K., Wei, W., Ariga, K., Lvov, Y., 2011. Natural tubule clay template synthesis of silver nanorods for antibacterial composite coating. ACS Applied Materials and Interfaces 3, 4040e4046. <u>https://doi.org/10.1021/am200896d</u>.
- 2. Albanis, T. A., Hela, D. G., Sakellarides, T. M., & Danis, T. G. (2000). Removal of dyes from aqueous solutions by adsorption on mixtures of fly ash and soil in batch and column techniques. Global Nest: Int. J, 2(3), 237-244.
- **3.** Ali, H., & Khan, E. (2017). Environmental chemistry in the twenty-first century. Environmental Chemistry Letters, 15(2), 329-346.
- **4.** Al-Khalaf, A.K. (2015). Green chemical applications: Highly efficient process on selective formation of industrial materials. Int. J. Curr. Res. Aca. Rev., 2, 15-19.
- **5.** Ankerfors, M. (2012). Microfibrillated cellulose: Energy-efficient preparation techniques and key properties (Doctoral dissertation, KTH Royal Institute of Technology).
- 6. Anyakora, C., 2007, Polynuclear Aromatic Hydrocarbons, in Leo M. L. Nollet (ed.), Handbook of Water Analysis, 2nd ed., CRC Press, New York, pp.579-598.
- **7.** Aono, M., Bando, Y., Ariga, K., 2012. Nanoarchitectonics: pioneering a new paradigm for nanotechnology in materials development. Advanced Materials 24, 150e151. <u>https://doi.org/10.1002/adma.201104614</u>.
- 8. Aprajita, P. N., & Sharma, R. S. (2011). A study on the lung function tests in petrol-pump workers. J Clin Diag Res, 5(5), 1046-1050.
- **9.** FREIRE, P. A. C.; TRANNIN, I. C. B.; SIMÕES, S. J. C. (2014) Bombeamento e tratamento da fase livre em Aquífero Litorâneo. Engenharia Sanitária e Ambiental, 19 (4). p. 461-470.
- **10.** ROCHA, L. P. et al. (2014) Use of personal protective equipment by gas stations workers: a nursing contribution. Texto&Contexto Enfermagem, 23 (1). p. 193-202.
- **11.** EMARA, A. M. et al. (2010) Immunotoxicity and hematotoxicity induced by tetrachloroethylene in Egyptian drycleaning workers. Inhalation Toxicology, 22 (2). p. 117-124.
- **12.** PEREZ-RIAL, D. et al. (2009) Temporal distribution, behavior and reactivities of BTEX compounds in a suburban Atlantic area during a year. Journal of Environmental Monitoring, 11 (6). p. 1216-1225.
- **13.** TERRÉS, I. M. M. et al. (2010) Assessing the impact of petrol stations on their immediate surroundings. Journal of Environmental Management, 91 (12). p. 2754-2762.
- 14. Larsen, J. C., & Larsen, P. B. (1998). Chemical carcinogens: In: RE Hester and RM Harrison (eds) Air Pollution and Health (pp. 33-56).
- 15. Gary, J. H., Handwerk, G. E., & Kaiser, M. J. (2007). Petroleum refining: technology and economics. CRC press.
- **16.** Grieshop, A. P., Marshall, J. D., & Kandlikar, M. (2011). Health and climate benefits of cookstove replacement options. Energy Policy, 39(12), 7530-7542.
- **17.** Bizzo, W. A., de Calan, B., Myers, R., & Hannecart, T. (2004). Safety issues for clean liquid and gaseous fuels for cooking in the scope of sustainable development. Energy for Sustainable development, 8(3), 60-67.

- **18.** Kolahalam, L. A., Viswanath, I. K., Diwakar, B. S., Govindh, B., Reddy, V., & Murthy, Y. L. N. (2019). Review on nanomaterials: Synthesis and applications. Materials Today: Proceedings, 18, 2182-2190.
- 19. Joussein, E., Petit, S., Churchman, G.J., Theng, B., Righi, D., Delvaux, B., 2005. Halloysite clay minerals a review. Clay Minerals 40, 383e426. <u>https://doi.org/10.1180/0009855054040180</u>.
- **20.** Ruiz-Hitzky, E., Aranda, P., Darder, M., Rytwo, G., 2010. Hybrid materials based on clays for environmental and biomedical applications. Journal of Materials Chemistry 20, 9306e9321. <u>https://doi.org/10.1039/C0JM00432D</u>.
- **21.** Viseras, C., Cerezo, P., Sanchez, R., Salcedo, I., Aguzzi, C., 2010. Current challenges in clay minerals for drug delivery. Applied Clay Science 48, 291e295. <u>https://doi.org/10.1016/j.clay.2010.01.007</u>.
- **22.** Al-Khalaf, A.K.H. (2012). Effect of solid catalysts on selective formation of naphthalene derivatives, PhD Thesis, Cardiff University, Wales-UK, 2012.
- **23.** Smith, S., Al-Khalaf, A.K.H., El-Hiti, G.A., Pattisson, S., (2012). Highly regioselective di-tert- amylation of naphthalene over reusable H-mordenite zeolite, Green Chem., 14, 1103-1110. <u>https://doi.org/10.1039/C2GC16443D</u>
- 24. Turbak, A. F., Snyder, F. W., & Sandberg, K. R. (1983, January). Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. In J Appl Polym Sci Appl Polym Symp (Vol. 37, No. 9, pp. 815-827).
- Hubbe, M. A., Rojas, O. J., Lucia, L. A., & Sain, M. (2008). Cellulosic nanocomposites: a review. BioResources, 3(3), 929-980.
- **26.** Siró, I., & Plackett, D. (2010). Microfibrillated cellulose and new nanocomposite materials: a review. Cellulose, 17(3), 459-494.
- 27. Harthcock, M. A., & Atkin, S. C. (1988). Imaging with functional group maps using infrared microspectroscopy. Applied spectroscopy, 42(3), 449-455.
- **28.** Choo, L. P. I., Wetzel, D. L., Halliday, W. C., Jackson, M., LeVine, S. M., & Mantsch, H. H. (1996). In situ characterization of beta-amyloid in Alzheimer's diseased tissue by synchrotron Fourier transform infrared microspectroscopy. Biophysical Journal, 71(4), 1672-1679.
- **29.** Prabhu, P. P., & Prabhu, B. (2018). A review on removal of heavy metal ions from wastewater using natural/modified bentonite. In MATEC Web of Conferences (Vol. 144, p. 02021). EDP Sciences.
- **30.** Nowack, B., & Bucheli, T. D. (2007). Occurrence, behavior and effects of nanoparticles in the environment. Environmental pollution, 150(1), 5-22.
- **31.** George A. Olah; Arp´ad Moln´ar; G. K. Surya Prakash: Hydrocarbon Chemistry, Wiley & Sons, Inc., USA, Third Edition, 2018.
- **32.** Lvov, Y., Wang, W., Zhang, L., Fakhrullin, R., 2016. Halloysite clay nanotubes for loading and sustained release of functional compounds. Advanced Materials 28, 1227e1250. https://doi.org/10.1002/ adma.201502341.