

JOURNAL OF CHEMICAL ENGINEERING



THE INSTITUTE OF ENGINEERS, BANGLADESH (IEB)
CHEMICAL ENGINEERING DIVISION

Journal of Chemical Engineering

Vol. ChE 31, No. 1, January 2023



The Institute of Engineers, Bangladesh (IEB)
Chemical Engineering Division

**Journal of Chemical Engineering
The Institute of Engineers, Bangladesh (IEB)**

Vol. ChE 31, No. 1, January 2023

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Cover Page and Graphics: Raihan Ahmad Ashrafi

Printing Press: Bornomala Printing Press, Dhaka, Bangladesh.

Date of Publication: 30 April 2023

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Chemical Management and Safety: Growing Concerns of Chemical Accidents in Bangladesh

Easir A. Khan*, Enamul Haque, Fahim Shahriar Sakib and Muhit Kabir Sarneabat

Department of Chemical Engineering, Bangladesh University of Engineering and Technology,
Dhaka-1000, Bangladesh,

Received: 13 September 2022; Accepted: 3 December 2022; Published: 30 April 2023

Abstract: A number of catastrophic events occurred in the chemical industries, chemical warehouses, transportation and distribution facilities in recent years, resulting in many deaths and substantial collateral losses. The government subsequently drafted and reconsidered safety regulations and intervene the management of chemicals to ensure protection of public safety and security. This study addresses key research points as (a) How to ensure safety and security of the critical chemical facilities? and (b) What are the key steps required to implement an effective chemical safety management system in Bangladesh? Four recent tragic chemical accidents are analyzed to understand the causes and consequences. The research article presents critical observations of each incident and the key lessons learned from those accidents. The research particularly focuses on the identification of priorities, formulation of national action plan, recommendations for improving national chemical management system and prevention of chemical accidents. The findings of this study and recommendations will be helpful for safety professionals, industry stakeholders, regulatory agencies, and policy makers for effective chemical management in chemical facilities and process industries in Bangladesh.

Keyword: Chemical Management, Chemical Accidents, Chemical Safety, Fire and Explosion, Lessons Learned and Bangladesh

1. Introduction

The ever-expanding manufacturing sector is the driving force behind the country's GDP expansion, which has resulted in a significant increase in chemical demand over the last decade. The risks associated with chemical facilities are often greater in a country like Bangladesh. The key players here seldom prioritize the safety concerns. The economy of Bangladesh is portrayed as a developing market economy in the world. Recently, Bangladesh was promoted to the community of middle-income countries. From the last decade she has inspired other countries which are underdeveloped by economic growth and sustainable development. Around 209 billion USD increased as Gross Domestic Product (GDP) in the last decade with the growth rate of around 5.5%. Before the COVID pandemic, the GDP growth rate was the highest in the value of 8.15%[1]. Such a higher growth rate was achieved due to the development of micro credit and the manufacturing sectors. The main players in the manufacturing sectors are the garment industries, fine chemicals industries, pharmaceuticals, plastics, tannery and consumer goods industries etc [2]. The demand of chemicals has substantially increased to continue their steady and sustainable growth. Bangladesh is now working and envisioned to achieve all SDG goals by 2030. It is important to note that ensuring workplace safety, chemical safety and security, industrial and process safety, pollution prevention have a significant relationship with several SDGs i.e. affordable and cleaner energy for safer environment [SDG 07], decent work and economic growth [SDG 08], sustainable cities and communities [SDG 11], and climate action [SDG 13]. Unfortunately, chemical safety and security issues are often ignored and are in the list of national priorities. Very few works have been reported on chemical safety and security issues in the context of Bangladesh. The current practices and prospects of chemical safety and security management in textile industries of Bangladesh had been reviewed by Haque et. al. [3]. Chemical Industries in Bangladesh are having serious safety deficiencies in various level [4]. Consequently, the rate of chemical accidents is increasing day by day as shown in Figure 1 (reported in national newspapers). The number of chemical accidents is increased significantly in year 2021 which caused many fatalities, significant loss of properties and impact on the business performance and economy of the country. The numbers often do not reflect the true scenario as many of the accidents are not reported properly.

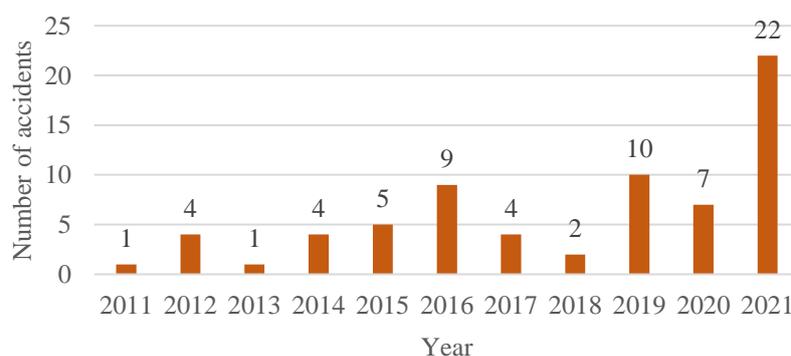


Figure 1. List of tragic chemical accidents reported in national newspapers in year 2011 - 2021

* Corresponding Author: Easir A. Khan,
E-mail: eakhan@che.buet.ac.bd

Table. 01. Major catastrophic chemical accidents in Bangladesh [2016-present]

Time	Location	Events	Consequence	Short Description
June 2016	Tongi, Gazipur	Hydrocarb on fire	7 fatalities and several injuries	A fire erupted after a boiler exploded at the factory of Smart Metal and Chemical Industries in Gazipur. The factory produced furnace oil from old tyres which did not have any license and legal documents.
2016	Chittagong	Ammonia	250 injured from toxic exposure	An explosion occurred at the factory of a 500-ton liquid ammonia tank located in Anwara upazila of Chittagong. The tank contained more than 325 tons of liquid ammonia at the time of the explosion. A huge gas cloud is formed and dispersed into the air. The toxic ammonia gas spread over several kilometers and wind carried away the gas to the other bank of the Karnaphuli River leaving nearly 250 people fell sick inhaling the toxic ammonia gas
2016	Gazipur	Fire	43 fatalities and more 70 injuries	A fire and explosion occurred in a plastic packaging factory named Tampaco Foils in Tongi BSCIC industrial town of Gazipur. After the explosion, the ceiling and walls of the factory collapsed which killed 43 people, including two pedestrians. Fire service professor took more than 48 hours to control the fire as huge amount plastic resin and flammable raw materials were inside the factory premises.
2019	Old Dhaka	Fire and Explosion	71 fatalities and hundreds injured	Known as churihatta tragedy. An explosion occurred in 1 st floor of wahid mansion. A chemical warehouse where huge amount of flammable and combustible chemicals was stored. After the explosion, these chemicals spread all over after the explosion and fire massive fire engulfed the nearby roads. People were stacked there due a heavy traffic and died in the fire.
2019	Keranigonj	Fire	22 fatalities and 16 injuries	The devastating fire sparked by a LPG release from cylinders had gutted the Prime Pet and Plastic Industry factory. Peoples working inside the factory were unable to evacuate and burnt to death.
2019	Gazipur	Fire	10 dead and 15 injured	The fire broke out on the top floor of the three-storied building at a luxury fan factory in Gazipur. Flammable solvent was stored and used for painting work. Four units of firefighters doused the fire after one-and-half hours of frantic efforts. Most of the bodies were charred beyond recognition.
2020	Narayanganj	Fire and Explosion	34 death and several other injured	The explosion, triggered by a gas leak, ripped through Baitus Salat Jame mosque at once bewildering the pilgrims. The glasses of the door and windows were shattered in the blast. The leaking pipeline might have caused gas to accumulate inside the Mosque, and a spark then probably led to the explosion. It produced intense heat and critically burned the over 40 peoples.
2021	Dhaka	Fire	4 dead and 24 injured	A fire broke out at a chemical warehouse in Armanitola of Old Dhaka. The fire started at the ground floor of a six-storey building named Haji Musa Mansion at 3:18am. The fire later spread quickly due to the presence of combustible material stored in the eight to ten warehouses on the ground floor of this building and the whole building was engulfed in smoke. People trapped inside who were residing the building in the upper floor.
2021	Gazipur	Fire	3 dead and 22 injured	Fire damaged most parts of the hydrogen peroxide of SM Chemical. The factory produced and stored hazardous chemicals including hydrogen peroxide, chlorine, bleaching powder, caustic soda, etc. The fire service officials suspected that the fire broke out following an explosion in the storage facility for hydrogen peroxide. There was a huge explosion at the factory, causing spread of toxic gases in the area and shattering windows of around 50 adjacent buildings.
2021	Dhaka	Explosion	11 fatalities and 100 injuries	The blast took place on the evening of 27 June at the ground floor of a three-storey building in the Moghbazar area of Dhaka. The Fire Service and Civil Defences suspected that the explosion

Time	Location	Events	Consequence	Short Description
				occurred due to the accumulated methane gas from leaked pipelines. The blast wave destroyed the ground floor and 3 buses that were crossing the front side of the building
2021	Narayanganj	Fire	52 killed and 100 injured	The devastating accident took place on 08 July 2021 due to improper storage of highly flammable chemicals, plastic resin, packaging and other combustible materials. A 35,000 square-foot warehouse was being used for production, with no minimum fire safety. Workers trapped inside the factory and died due to fire and toxic smoke inhalation.
2021	Bagura	Fire	5 dead and several injured	The fire broke out around 11:30 am in the BIRS Disposable Plastic Factory in the Santahar, Bagura. Ten units from the Bogura and Naogaon Fire started from a factory machine explosion. Fire Service were managed to get the blaze under control after nearly three hours effort. The damage from the fire was claimed about Tk 250-280 million.
2021	Jhalakati	Fire	40 fatalities and 100 injured	A fire broke out on the Barguna-bound MV Avijan-10 launch carrying approximately 800 passengers from Dhaka, off the coast of Jhalakathi on 24 December 2021. After two hours of frantic efforts, the fire was brought under control. According to the Barishal Divisional Fire Service, the fire might be started in the engine room where fuel was stored and quickly spread as the ferry travelled along the river Sugandha.
2022	Chittagong	Fire and explosion	51 dead including 13 fire service professionals and over hundred injured	The first smoke was detected on Saturday 4 June at 9:00 pm from a container of the BM Container Depot. Twenty personnel from two fire service stations initially tried to control the fire by water spraying. At approximately 10:30 pm, a container exploded with a loud noise razing everything within 100 meters of the front from the center of the explosion to the ground instantly. About 12000 m ² container freight station destroyed completely. The explosion shook the neighborhood and shattered glasses of windows of nearby houses. Firefighters brought the fire under control after three days of the explosions.

After each fatal chemical accidents, questions were raised on the poor performance of regulatory authorities. The demand for effective regulations and management of chemicals and chemical facilities has increased. However, very little progress has been made so far. Table 01 shows the recent accidents and its consequences. The accidents took many lives, destroyed properties and facilities, interrupted the business and country's economic growth. Many of those accidents occurred for just not following safety procedures and guidelines [5]. Several committees were always formed to investigate the accident by different agencies, ministries and regulatory authorities. The findings and learnings from those accidents had not been made public. In most cases, investigation committee focused particularly on the immediate causes of the accidents. The root or underlying causes of the incidents had often been ignored. Unfortunately, the similar events or accidents are recurring. There has been some improvement of safety standards and practice especially in textile sectors due to the client/buyer pressure, but these are not seen in other chemical intensive industrial sectors. The uncultivated culture and lacking safety procedures in chemical sectors caused accidents including fire, explosion, toxic release etc.

In recent years, fire accidents have happened frequently bearing high mortality, huge economic loss and environmental damage [6]. The examples of recent accidents are like BM container depot fire and explosion, Hashem food industries fire, Moghbazar blast, Churihatta fire and explosion, Tampaco fire and explosion and Narayanganj mosque explosion as described in Table-01. Such accidents shook the heart of people all over the country and made people rethink the establishment of proper and effective chemical safety management. Such accident will repeat unless the intervention or necessary steps are taken by the key stockholders involved in managing hazardous chemicals. The regulatory standards, guidelines, role of regulatory authorities were reviewed and a framework of sound management chemicals in Bangladesh was proposed by Prof. Syeda[7]. In this article, the four tragic chemical accidents are analyzed critically to understand the causes and deficiencies. The analysis aims to find out the needs for improvement in the area of hazardous chemical storage, use and transportation and to prevent chemical accidents. The study also focuses to identify the key stakeholders and prepare national action plan recommendation for effective management of chemicals. The national standards and guidelines had been reviewed to identify the gaps and needs related to chemical safety of chemical and process industries.

2. Case Studies: Chemical Catastrophe in Bangladesh

The major chemical accidents in past five years are described in Table 01. Some of these accidents were disastrous and exposed the vulnerability to manage chemical safety, lack of awareness and safety cultures in Bangladesh. Here, four recent tragic chemicals accidents occurred are discussed and analyzed in this section to understand the causes, consequences and lessons learned.

2.1 BM Container Depot Fire and Explosion: June 04, 2022 (Chittagong)

A devastating explosion occurred on the night June 04, 2022 at BM Container depot situated in 20 km away from Chittagong port which took away 51 lives including 13 fire service professionals and damaged the BM container facilities. The origin of fire was presumed from a container loaded with hydrogen peroxide that was kept in the yard for export. There were 533 containers in total and 37 of them contained 50%-60% of hydrogen peroxide. The estimated amount of hydrogen peroxide is 20,400 kg in each container. Out of 37 containers, 25 containers were damaged in the fire incident. A container was exploded with a huge bang about 1.5 hours after the fire was initially detected by depot security personals [8].

Primary investigation suggested that the origin of fire and explosion caused by the hydrogen peroxide containers. The exploded container was placed horizontally along the east-west direction. The explosion was so powerful that it had created a 15-20 feet crater at the center. The container freight station located 30 meters from the front was extensively damaged. Figure 2 shows the intensity of the damage due to explosion.



Figure 2: Damaged containers and freight station due to explosion

The powerful explosion produced a strong blast wave that shattered the structures and window glasses up to around 4 km distances. The container was fragmented into small pieces due to the explosion and flying debris travelled over hundreds of meters with high velocities. Such a powerful explosion had not been possible without the presence of chemicals. The detonation might have occurred due to the confined space explosion or boiling liquid expanding vapor explosion. People died mainly from direct blast impact or because of the impact from the flying debris. Some of them were critically injured and unable to evacuate the site and later charred as fire intensified after the explosion. People living nearby were also exposed to hydrogen peroxide vapor, mist or liquid and got severe skin and eye injuries. Some were experiencing hearing problems due to the blast effect. Hundreds of people got hospitalized because of their injuries.

Bangladesh had never experienced such catastrophic accidents where 13 fire service professionals have lost their lives in a single incident. On August 4, 2020, at precisely at 6:07 pm, a cache of 2750 tons of ammonium nitrate exploded at the Beirut Port minutes after a firework, the warehouse had caught fire which is the largest non-nuclear explosion of modern times [9]. The explosion destroyed the port facilities and half of the Beirut city. However, explosion of BM depot was quite unlikely to happen. BM container depot usually handle all export items and licensed for low risk imported products. However, BM depot stored hydrogen peroxide container loaded with 20.4 ton of 50% hydrogen peroxide solution in the container yard for export. Hydrogen peroxide (50% solution) is strong oxidizing chemicals and considered as Dangerous Goods (DG) (UN 2014) as per IMDG Code. Hydrogen peroxide may cause fire in contact with metal or flammable materials. Moreover, it may decompose slowly and generate extensive heat to create fire even without presence of an ignition source.

As containers were exposed to fire, hydrogen peroxide decomposed rapidly and produced extreme heat and pressure inside the containers and subsequently caused explosion. Using TNT equivalency [10] method and consequence analysis, the intensity of the explosion was estimated equivalent to detonation of 150 kg - 200 kg of TNT. The explosion released huge amount of energy which created a powerful shock wave and flying fragments. The sources of energy were basically from a) the external fire, b) the internal fire due to presence wooden support materials inside the containers and c) the exothermic decomposition reaction of hydrogen peroxide. After the explosion, fire intensified and propagated as hydrogen peroxide spread all over the container yard and container freight station. The damaged

hydrogen peroxide jars were found all over container yard, evident from Figure 2. Fire service professionals relentlessly worked for four days to extinguish the fire completely.

The BM depot accident gave a wakeup call regarding the chemical safety issues, possible consequence, lack of knowledges, awareness and management system. Some critical observations on BM container depot fire and explosion are given below.

- The BM depot explosion was a preventable accident and quite unlikely to occur. The event could be prevented if the storage guideline for storage of oxidizing chemicals was followed. The IMDG code and CPA traffic guideline clearly mention the potential fire and explosion hazard of oxidizing chemicals, such as 50% hydrogen peroxide solution.
- BM depot is a private inland container depot (ICD) approved by ministry of shipping and Chittagong port authority to facilitate export and import of low-risk items. Private ICDs are mainly involved to handle all export goods, low-risk imported products and not authorized for Dangerous goods.
- Bangladesh did not export any DG goods in the past. However, it started exporting hydrogen peroxide thorough private ICD as they are eligible for all exporting items. The container depot is under regular inspection by regulatory authorities like CPA and Ministry of Shipping. However, responsible authorities failed to identify the potential hazard of handling dangerous goods (hydrogen peroxide) in Private ICD. Private ICDs are not equipped and structured for handling DG items.
- BM depot were not aware about potential fire and explosion hazards of hydrogen peroxide. Hydrogen peroxide containers were stored together with other combustible items, locked, and kept in container yard at hot sunny weather.
- BM depot did not have personnel to oversee the safety and security issues of its activities in chemical storage and handling. BM depot did not have its own firefighting capability and standard operating procedure (SOP) for emergency response. The depot had to wait for arrival of fire service professional from FSCD to extinguish the fire. Due to the lack of ERP, instead of immediate evacuation, people were engaged taking photos, live streaming of the fire scene which were main reason for so many casualties.
- Fire service professionals were unable to extinguish fire as fire was inside the container. They were trying cool the container with water spray. Fire service professional were not trained enough to evaluate risk of potential explosion. There were series of small explosion with loud sound inside the container. These loud sounds were due to explosion of 30 kg of plastic jar containing hydrogen peroxide. This was a clear indication of large-scale explosion from confined container. Fire fighters were closer when the container exploded and 13 of them lost their life due the blast effect.

2.2 Fire Tragedy at Hashem Food Industries: 8 July, 2021 (Narayanganj)

On July 8, 2021, a deadly fire razed Hashem Foods Limited in Rupganj of Narayanganj and killed at least 52 workers and staffs of the factory. Fire originated at ground floor of the five storied building and people at the upper floor were trapped and were unable to evacuate. 49 bodies were found at third floor as the escape route was locked with a latticed gate at the back [11]. The poor workers took shelter in an air condition room and were asking for help. Deaths were mainly caused by inhalation of toxic smoke and lack of oxygen. The bodies were later charred due to fire spreading at the floor. Figure 3 shows the black smoke scaping off the building due to fire. Unfortunately, people were trapped and burnt alive for at least three hours inside the fire-blazed building.



Figure 3. Black, thick and toxic smoke produced from Hashem food industry fire

A vast amount of flammable and combustible chemicals and plastic raw materials were stored at the ground floor. Fire spread quickly and smoke blocked the evacuation routes. According to several local and international media, the factory employed approximately 7000 workers in its 35000-square-foot building with only two staircases, which were not adequate enough for emergency evacuation. There was no emergency staircase in the building. Moreover, the escape route at third floor was locked. There were no smoke detectors, fire alarms or emergency exits anywhere in the six-story building. The occurrence of fire at hashem food industry fire demonstrate the reflection of our industrial

safety standards and monitoring performance of regulatory authorities in Bangladesh. The critical observations on hashem food industries fire are given below.

- Hashem food industry fire tragedy was a preventable accident. The industry does not have safety personnel and minimum safety procedures at their factory.
- The same building housed different categories of production process. A pipeline system that carried edible oil; the large quantity of paper and plastic raw materials stockpiled on the premises.
- Both gates on the third floor were locked making it impossible for workers to flee which was very unfortunate. This clearly indicates the poor performance of monitoring agency especially Department of Inspection for Factories and Establishments (DIFE), and the Fire Service and Civil Defence (FSCD).
- No emergency response plan (ERP) existed in the factory. Workers were trapped inside the factory for hours and fire service professionals were unable to rescue them alive. The strength and capability of fire service personnel were also questionable.

2.3 Moghbazar Blast: 27 June 2021 (Dhaka)

The strong blast took place on the evening of 27 June 2022 at the ground floor of a three-story building in the Moghbazar area at the capitalcity, Dhaka. Twelve people died in the incident and over hundreds got injured. The explosion destroyed the ground floor and the windows of seven buildings nearby were shattered. Figure 4 shows the intensity of damage caused by the blast.

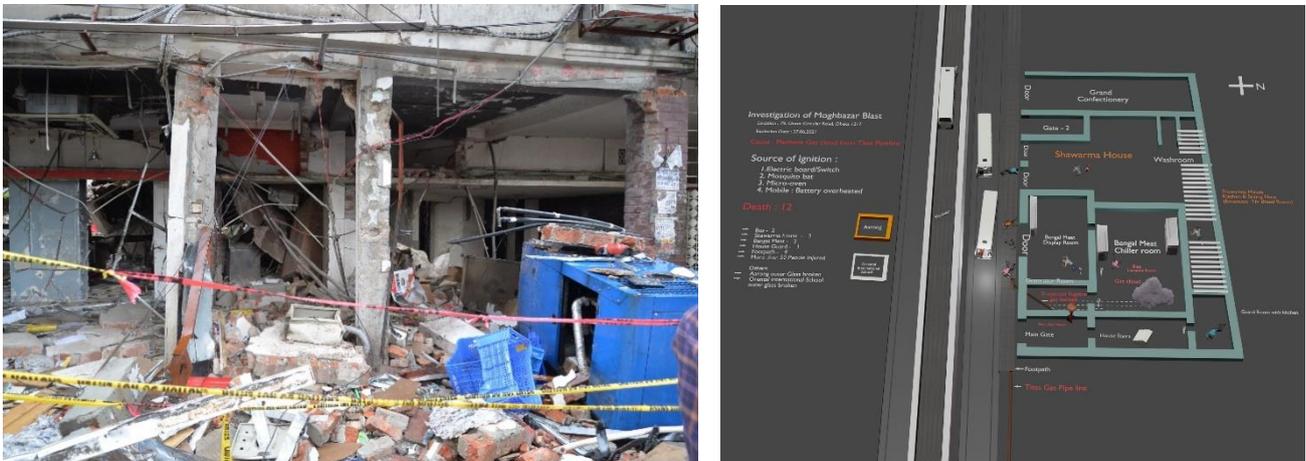


Figure 4. Ground floor of a building collapse due to a strong explosion

Three buses were also shattered due to the explosion. People died who were crossing the road and working in affected shops. A passenger also died in the accident who was riding a bus on the flyover crossing the blast zone. Referring to fig. 4, Brick wall of zone A and B damaged completely. The roof of zone A collapsed. From consequence analysis, the estimated amount of natural gas required for such explosion is 3.0 kg. The explosion intensity is estimated equivalent to detonation of 1 kg of TNT [10]. The blast pressure produced is calculated using TNT equivalency method and their effects are given in Table 02. Minor structural damage was observed in ARONG building about 200 ft away from the Bengal meat shop. Complete destruction was observed in Bengal meat chiller room in the area A as shown Figure 4.

Table 02: Blast pressure and its effects at different distance from the explosion center.

Distance ft from the center of the explosion	Area circled in Fig. 4	Blast Pressure kPa	Effects
10		106.37	Probable complete destruction of building
20	A	50.65	Brick panel of 8-12 inch thick failed
50	B	10.13	Steel panel of clad building slightly distorted
80	C	7.09	Partial demolition of houses
120		5.07	Large and small windows usually shatter
200	D	3.04	Limited and minor structural damage

The natural gas accumulation inside the Bengal meat chiller room might be a reason to form a flammable mixture which later detonated. There was a natural gas pipeline riser which passed thorough the building and placed next to the stairs. The Fire Service and Civil Defence claimed that the explosion took place due to the accumulated gas. However,

they failed to pinpoint the sources of the leaked gas. An official of the explosives department, on condition of anonymity, said that there is evidence that the gas which caused the explosion came from a leaked Titas pipeline [12]. The inquiry report submitted by Titas mentioned that Titas had no liability in the accident as there were no gas connections in the building. The abandoned riser was mentioned, but no details were given. The accidents reflect the potential danger of fire and explosion from urban gas pipelines leakage. The critical observations of the accident are discussed below.

- Several investigation committees were formed after the accident and their findings were contradictory to each other. Some findings are not scientific and baseless i.e sewerage gas, LPG cylinders which were found in shwarma house, a restaurant nearby the explosion area.
- No organization admitted that they might have deficiencies or issues considered to be corrected for prevention of such accidents
- Gas pipeline leakages are in common scenarios in urban areas in Bangladesh. The probability of natural gas riser leakage found about 10% from a study conduction Karnaphuli Gas Distribution Company Limited (KGDCL) has been a great concern for public safety.

2.4 Churihatta Fire and Explosion: 20 February 2020 (Old Dhaka)

On the night of 20 February 2019, a devastating fire and explosion occurred at Churihatta area in Chawkbazar, Old Dhaka causing over 71 deaths and numerous injuries. Total 37 fire-fighting units worked incessantly for 15 hours to extinguish the fire [7]. There was a huge traffic at the adjacent road due to the closure of some roads at that night. A deadly fire erupted from a sudden explosion at the 1st floor of wahid mansion. A huge amount of highly flammable, body spray, perfume and different types of oil were stockpiled inside the building. The 5-inch thick external wall of the storage building collapsed during the explosion and highly pack flammable material spread all over the adjacent roads as shown in Figure 5. A massive inferno caused by the blast engulfed the traffic, trapped people and burnt to ashes. Many took shelter in a narrow space on the ground floor where they died due to oxygen deficiency and toxic vapor inhalation.



Figure 5. Fire and explosion scene of Churihatta tragedy

After the incident, different agencies including the Ministry of Industries, Ministry of Home Affairs, Ministry of Labour and Employment (MoLE), FSCD, and Dhaka South City Corporation (DSCC) formed investigation committees to find out the causes of the accident. However, the opinion from the different committee contradicted with each other. The probe committee of Ministry of Industries submitted a report claiming the fire was sparked by a gas cylinder blast on the road and that the explosion of a roadside transformer contributed to it. Contrarily, the probe committee of Ministry of Home Affairs reported that the fire originated from a chemical explosion on the first floor of Wahed Mansion, the worst affected building, where hundreds of damaged cans of body spray and canisters to refill gas lighters were found. The latter view was supported by most other probe committees.

Initially, after the news of the inferno spread, people mistakenly assumed that a cylinder blast in Rajmahal Hotel and Restaurant had caused the fire. Footage from Rajmahal's closed-circuit camera later helped to reveal that the fire broke out from the 1st floor of the adjacent five-storey Hazi Wahed Mansion resulted from a confined space explosion. Somehow, a vapor-air explosive mixture was formed inside the room either from hydrocarbon gas or volatile organic chemicals used in perfume or body spray. The explosive mixture later ignited and exploded with massive fireball. In addition, another video showed air-freshener canisters falling onto the street during the blast. The fire later spread quickly due to presence of plastic goods and other flammable items, preserved in the adjacent warehouses. The Fire Service and Civil Defence's probe body found the warehouses on the first, second and third floors contained huge quantities of body spray, high pressure deodorant canisters, raw plastic granules, air freshener, aerosol, gas lighter, fuel, etc. The Criminal Investigation Department of police found ethanol,

butane, isobutene, propene, butoxyethanol, glycol ether, diethyl phthalate, propylene and polyethylene – among the seized products, all flammable products were found on the spot. The critical observations are listed below.

- Storage of highly flammable chemicals in residential building was the key contributing factor of this accident. Release of small amount of these chemicals may have formed explosive mixture with air in a confined area and could have caused explosion.
- Chemical factories and warehouses in residential building is serious concern for public safety, especially unplanned urban area like old Dhaka. According to an estimate by Bangladesh Poribesh Andolan (Bangladesh Environmental Movement), more than 25 000 chemical warehouses are in Old Dhaka, of which some 15 000 are in residential buildings [7]
- Relocation of these chemical business from old Dhaka is very necessary. A project of BSCIC chemical industrial park had been initiated after Nimtoli tragedy (124 fatalities, 2010). However, the project is still ongoing and there location process has yet to start after a decade. It clearly indicates the lack of prioritization as government has completed many megaprojects within this timeframe i.e padma bridge.
- Many of these chemical businesses and establishments do not have valid license. This is much more concerning as they are not compliant as per national regulations. In many cases, the business has been identified illegal after the accident occurs. Thus, it is quite important to identify the illegal business and stop them functioning to avoid any future incident.
- Public safety should be prioritized rather than the business. However, it is evident that key stakeholders remained silent and have been continuing their unsafe business in residential area even risking their own lives

3. Lessons learned

Every accident provides some opportunities to learn. Recurrence of similar accident shows a clear sign of failure to learn lessons from the accidents. The perfect example of such failure is Beirut port explosion in 2020. A huge quantity of ammonium nitrate was stored for 7 years at Beirut port. During this time, a similar explosion was happened in Chinese Tianjin port in 2015. Beirut explosion could have been prevented if Beirut port authority had learnt lessons from Tianjin explosion [13]. If the safety incidents were properly investigated and lessons learned were shared with the relevant organization, recurrence of accidents could have been prevented with necessary control measures. The root causes are almost the same in most chemical accidents in global context. The key lessons learned from the accidents discussed in previous section are presented below.

3.1 Management of Change

The key principle of management of change is to conduct risk analysis and make risk-based decision making before making any changes. In the case of Sitakunda BM Depot accident, the high-risk DG items export through private ICD has not been approved through proper procedures considering safety and security issues. Private ICDs are licensed for handling and storing of empty container, temporary storage of selected low risk import items and all export goods. This indicates that private ICDs are not approved or designed to handle high-risk items or dangerous goods (DG). Bangladesh do not export any high-risk goods and so ICDs allowed for all export goods. However, customs provide permission to private ICDs for storing and handling of DG goods like hydrogen peroxide as an export item (not considering its inherent risk). Therefore, management of change must be effectively implemented before making any changes related to DG storage, handling and use.

3.2 Cost of Negligence and Noncompliance

Organization often ignores safety due to its additional cost of implementation. Sometimes these are from negligence. Father of safety in chemical engineering, Trevor Kletz famously reported as “there’s an old saying that if you think safety is expensive, try an accident”[14]. Accidents cost a lot of money. A perfect example for cost of negligence is Hashem food industry fire accident which took 52 lives. Accidents are not acts of God; every accident is preventable if people do the right things.

3.3 Emergency Management Plan

Organization must have its own emergency management plan. In cases of BM depot explosion and Hashem food industry fire, it was apparent that both organizations did not have emergency management plan. Tragic loss of lives could have been avoided or reduced significantly if the management had evacuated their staffs and workers in time. In BM depot fire and explosion, many died or critically injured who were just watching, taking picture, or making live streaming of the fire scene.

3.4 Risk-based Decision in Emergency Response

In BM depot explosion, 13 fire service professionals lost their lives while performing their duties. They were conducting aggressive firefighting from a very close distance and unaware of potential explosion hazard from closed containers. Fire service professional must have necessary expertise to assess the potential risk while doing their job.

There were clear indications of explosion hazard during the BM depot fire i.e. a) closed container is always prone to explosion, b) presence of Hydrogen peroxide, a strong oxidizing chemicals has explosion hazard in confined space, c) Series of small explosion with a loud bang observed from the container during the firefighting. This unfortunate loss of life could have been avoided if they had assessed the explosion risk beforehand and taken defensive firefighting approach. Therefore, expertise of fire service professionals needs to be enhanced in the area of technical knowledge on fire and explosion, risk assessment and risk-based decision making during the emergencies.

3.5 Lack of coordination in Accident Investigations

As discussed in previous section, immediately after the catastrophic accident, different regulatory agencies, ministries and organizations forms probe committees. These committees usually make a visit to the site and produce a report within very short period. Many of this committees do not publish their report. They often provide their opinions on print and electronic media. In many cases, their findings and opinions contradict with each other [7]. It creates confusion to the public. The objective of these committees mostly focuses on the immediate causes of the accident not the underline/root causes. Human, organizational, regulatory and 'cultural' shortcomings are identified as underlying causes of major accidents in safety critical industries [14]. Dr. Kletz says that accident prevention should be about looking for root causes, and not individual blame: "For a long time, people were saying that most accidents were due to human error and this is true in a sense but it's not very helpful. It's a bit like saying that falls are due to gravity." [15]The objective of accident investigation should be focused on the underlying causes, shared the learning and recommendations with others so that organizations can take mitigative measures to prevent similar accident to occur in future. This objective has not yet been achieved in Bangladesh due to the lack of coordination and technical merit of existing accident investigation procedures. We strongly proposed formation of a 'National Accident Investigation Board' to conduct the accident investigation. The board will form a team comprises of expertise from relevant fields who will be responsible for accident investigation, find out root causes of the accident and prepare recommendations for respective stakeholders, industries, and regulatory bodies.

4. National Guideline related to Chemical Safety

This section covers mainly rules, act, policy and guidelines related to the perspective of chemical management and safety.

4.1 Bangladesh labor law 2006

The Bangladesh Labour Act (2006) is the key labour legislation that sets Occupational Safety and Health standards, and compensation for injury and accidents in the workplace. In 2013, significant amendments were made to the BLA (2006), regarding occupational safety and health, primarily in response to the Rana Plaza collapse. The Bangladesh Labour Rules (2015) set implementation procedures to corresponding sections of BLA (2006).

4.2 OSH policy 2013

In the context of global, ethical and legal obligations to ensure a safe and healthy working environment for all, the National Policy on Occupational Health and Safety was formulated and adopted on 5th November 2013, with the understanding that the implementation of such a National Policy would firstly ensure the safety of workers and secondly, help increase industrial productivity. The Policy applies to all workplaces in Bangladesh, including formal and informal sectors of industries, factories, enterprises, business and commercial entities and farms.

4.3 The Environment Conservation Rules, 1997

The Environment Conservation Rules (1997) classifies industrial projects into four categories according to chemical process for purpose of license, prescribe the license requirements with procedures, issues declaration of ecologically critical areas and sets the standard values for different pollution parameters. The rules were developed under The Environment Conservation Act (1995) to protect the environment and ecological system from pollution of physical or chemical processes.

4.4 Explosive Rule 2004

Explosive Rules (2004) as well as The Explosive Act (1884), Explosive Substance Act (1908) deal with regulation of production, stock piling, transport, sale, use and importation of explosive chemicals. The explosive materials include gunpowder, nitroglycerine, dynamite, blasting powders and fulminate of mercury or of other metals.

4.5 The Dangerous Cargoes Act, 1953

The Dangerous Cargoes Act (1953) issued provision for the safety of port regarding working, transit and storage of hazardous cargoes including sulfur, tetrafluoroethane, calcium carbide, isobutene, liquefied gas etc. The act is legalized for ensuring the safety of ports, shipping companies and container depots which is enacted for preventing or dealing with explosions and fires on vessels carrying dangerous cargoes within the limit of any port.

4.6 The LPG Rules 2004

In order to ensuring safety of gas reservoir or cylinder, safety of liquefied petroleum gas, strong management and handling process, transportation procedure and storing process of the LPG gas in a cylinder, The LPG Rules (2004) is legalized.

4.7 The Petroleum Rules 2018

The Petroleum Rules (2018) as well as The Petroleum Act (2016) was enacted by Department of Explosives, Ministry of Power, Energy and Mineral Resource to control storage, transportation, distribution, refining, blending, testing, licensing and importation of petroleum products.

4.8 The Ammonium Nitrate Rules 2018

Ammonium Nitrate Rules (2018) is used to control the manufacture, stocking, packaging, sale, use, transport and importation of ammonium nitrate. Ammonium Nitrate is a fertilizer product which is also an explosive material under heating condition. The last incident happened on Beirut shook the Lebanon caused by this chemical agent in 2020.

4.9 The CNG Rules 2005

Under the Explosive Act (1884), the CNG Rules (2005) were implemented by Ministry of Power, Energy and Mineral Resource to ensure the safety of gas reservoir or cylinder, safety of liquefied petroleum gas, strong management and handling process, transportation procedure and storing process of the Compressed Natural Gas (CNG).

4.10 Bangladesh National Building Codes (BNBC 2020)

Bangladesh National Building Code (2020) was implemented to provide building design guidelines for residential, commercial, industrial and hazardous indoor facilities. Physical hazards as well as chemical hazards are considered in the codes. BNBC (2020) is implemented by Ministry of Housing and Public Works.

4.11 The Chemical Weapon (Prohibition) Act 2006

The Chemical Weapons (Prohibition) Act (2006) prohibits the development, acquisition, stock piling, production, transfer or use of discrete organic chemicals and schedule chemicals. Government of Bangladesh (GoB) decided to sign the Chemical Weapons Convention (CWC) on 14 January 1993. Bangladesh National Authority for Chemical Weapons Convention (BNACWC) was formed after enacting the Chemical Weapons (Prohibition) Act.

4.12 LPG Storage, Bottling, Transportation and Dispensing Codes and Standards, 2016

The Bangladesh Energy Regulatory Commission's LPG Storage, Bottling, Transportation and Dispensing Codes and Standards, 2016, deals with certifying quality and safety as well as environmental protection for LPG bottling, transportation, dispensing and storage.

4.13 Solid Waste Management Rules 2021

Solid Waste Management Rules (2021) was formed under the Environment Conservation Act (1995) to impose collection, recycling, disposal responsibilities on manufacturers of non-biodegradable products as well as the responsibilities of businesses included in solid waste management.

4.14 Air Pollution (Control) Rules 2022

The Ministry of Environment, Forest and Climate Change formed Air Pollution (Control) Rules (2022) to manage air pollution for environmental conservation and sustainable development. Air quality standards as well as emission standards from vehicles were set in the rules. The Department of Environment (DoE) is bound to prepare a National Air Quality Management Plan that involves an efficient management system and organizational working framework of indoor air quality.

5. Recommendations for Effective Chemical Management and Safety

The policy, rules and guidelines discussed in the previous sections are associated to some extent with chemical management and safety. However, standardized rules and regulation are yet to develop for chemical safety management in process industries. For effective safety management of hazardous chemicals, countries need to investigate the problem deeper and take a holistic approach for improving systems, existing practices and culture. The case studies discussed in the previous sections have revealed that current practices in chemical management have many levels of deficiencies. The weakness and challenges of effective chemical management are observed as,

- Absence of standardized rules, regulations, or procedures regarding chemical management
- Lack of widescale national or governmental coordination or integration of chemical safety and security
- Lack of financial resources or allocation in research for safer chemical management
- No centralized database for the identification, storage, and management of chemicals
- Unskilled, untrained, and unauthorized personnel handling hazardous chemicals
- Improper waste management
- Lack of chemical incident reporting means no immediate emergency response

- Lack of coordination in investigating chemical accidents
- Absence of a chemical safety culture
- Lack of awareness on risk of handling and transportation of hazardous chemicals

Chemical management and safety must be improved, and a safety culture should be built to prevent recurrence of chemical accidents. The objectives and methods of implementation for national action plan recommendations are given Table 3.

Table 3. Objectives and methods of implementation for national action plan recommendations

Objectives	Methods of Implementation
Standardization of rules and regulations on chemical safety management systems	Collaboration with local and international bodies and the creation of a central regulatory body for chemical security
Creation of a national authority for chemical management and safety	Formed after interactions with all stakeholders. Through stakeholder engagement program
Standardization of chemical storage and management practices	Through trainings and workshops from local and international experts
Standardization of and improvements to personnel training	Through regular trainings and monitoring from relevant experts and the development of SOPs for personnel
Increased government involvement towards chemical safety concerns	Increased engagement with relevant local and national government bodies
Stakeholder engagement program	Coordination with different regulatory agencies, industry stakeholder and academia
Regulatory Enforcement	Through regular inspection and monitoring
Establishment of National Accident Investigation Board.	Collaboration with local and international bodies, Coordination with different regulatory agencies
Awareness and Training	Through trainings and workshops from local and international experts
Chemical Safety Education	Establishment of a center of excellence in chemical safety research. Developing chemical safety courses in engineering curriculum
Emergency management	Develop SOP in collaboration with local and international bodies, Coordination with different regulatory agencies

6. Conclusion

The analysis of tragic chemical accidents reveals that Bangladesh is clearly lacking in different areas concerning chemical management and safety, i.e. standards and guidelines, risk analysis, risk communication, risk-based decision making, accident investigation, management of changes, research and development, safety education, training, safety awareness and emergency management. It is evident that chemical management system cannot be implemented only by standardization of rules and regulations. There must have to be clear national interest, strong regulatory enforcement, resource allocation, capacity building, awareness building and skilled manpower. The article presents the weakness and challenges concerning chemical management and provides national action plan recommendations with clear objectives and method of implementation to improve chemical management and prevent recurrence chemical accidents. The recommendations of this study can play a steering role to formulate a comprehensive national chemical management framework in Bangladesh.

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Crude Oil Spills Clean-up from Water Surface Using Modified Commercial Activated Carbon

S M Anisuzzaman^{1,2*}, Sariah Abang², Sara Elmira Binti Mohd Azraley²

¹Energy Research Unit (ERU),

²Chemical Engineering Programme, Faculty of Engineering,

Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, MALAYSIA.

Received: 15 March 2022; Accepted: 11 August 2022; Published: 30 April 2023

Abstract: Petroleum products and their derivatives are considered as a major source of pollution and spills of those products have devastating effects towards the environment. The objectives of this study were to modify the commercial activated carbon (AC) by impregnation method with 85% w/v phosphoric acid (H_3PO_4) solution and to remove crude oil spills from water surface using modified AC (MAC). Fourier transform infrared spectroscopy (FTIR) was used to check the functional group in the unmodified AC and MAC. The effect dosage of adsorbents, temperature and the effect of contact time towards the adsorption process has been carried out, where the results showed that MAC has a higher percentage of adsorption compared to unmodified AC. For the kinetic study, pseudo-first order was chosen for the best kinetic model to express the sorption of crude oil spills on MAC as it shows the R^2 value closest to 1. Meanwhile, for the adsorption isotherm, the result indicates that Freundlich was the most suitable model for describing the sorption equilibrium of crude oil on AC and MAC.

Keywords: Adsorption; modified activated carbon; crude oil spills; oil sorption capacity

1. Introduction

Due to exploration, transportation and production of petroleum fractions, oil spill causes various environmental pollution [1,2]. The impact of the oil spills can cause pollution towards four categories and these pollution are towards soil, aquatic systems, atmospheric pollution due to volatile components and lastly land-based spills of oil [3,4]. Coral reefs are one of the major fields affected by oil spills [5]. Other than reefs, humans can also be affected by oil spills. Due to variation of petroleum substances, such as gasoline, kerosene, diesel and petroleum waxes, different substances penetrate the skin at different rates. Some of the constituents of petroleum products are proven to be associated with being carcinogenic for instance benzene and some polycyclic aromatic hydrocarbons [3].

According to Demirel *et al.*, [6], there are four ways to combat oil spills which are burning, booms and skimmers, chemical dispersants and sorbents. Traditional methods often called for chemical dispersant methods to manage the oil spills. Generally sorbents are used due to their effectiveness, inexpensive, as well as safe. Adsorbents are promising methods for the removal of oil spill as compared to other methods when dealing with oil spills in water [1,6]. Adsorption capability can be depicted from cellulose based activated carbon (AC). The Adsorption capacities of the AC from alpha-cellulose was able to adsorb H_2S was 7.29 mg/g which is more than what methyl cellulose precursor can adsorb [7]. Doshi *et al.*, [8] conducted a study on the effectiveness of N,O-carboxymethyl chitosan for the removal of oil spills. Other than chitosan, natural adsorbents such as sawdust, straw, wool and peat also have been studied [9].

Activated carbon (AC) is an amorphous carbonaceous material derived from biomass, lignite and hard coal, synthetic materials and others. [10,11]. AC can be used as an effective adsorbent due to their high adsorptive capacity, high surface area and substantial pore volume. It can be used in a water treatment process, purification of air by removing the trace amount of unwanted substances [12]. AC can also be used to remove volatile organic compounds, namely benzene, toluene and methanol [13]. Modifications of AC are further made to increase surface adsorption and removal capacity [14,15]. According to Kim *et al.*, [16], impregnation of AC with phosphoric acid (H_3PO_4) results in a high adsorption capacity for selected volatile organic compounds such as benzene, toluene, p-xylene, methanol and etc. It has been also found that an increase in impregnation ratio will result in an increase in the ash content and percentage yield until it reaches an optimum value [15].

The objective of this study was to modify the commercial AC by impregnation method using H_3PO_4 and to remove crude oil spills from water surface using modified AC (MAC). Fourier transform infrared spectroscopy (FTIR) was used to check the functional group in the unmodified AC and MAC. The effect dosage of adsorbents, temperature and the effect of contact time towards the adsorption process has been carried out.

2. Materials and Methods

2.1 Preparation of AC using H_3PO_4

The AC (NORIT) was purchased from Sigma-Aldrich, which is a coconut shell based in powder form with ~100 mesh particle size. 85% of H_3PO_4 (Merck) was used for impregnation of AC. In the impregnation process, 10 g of AC was impregnated with 40% w/v of H_3PO_4 solution. The conical flasks containing the mixture were enclosed with aluminium foil. A few holes were punched onto the foil in order to let the vapours evaporate. Then, the mixture was set for three days to dissolve the solution by using a shaking water bath at standard room temperature. The chewy liquid was further dried at 120°C for 24 h in the oven. The impregnated AC was placed in a muffle furnace (Carbolite RHF 1500) at 500°C for 2 h for carbonization. After the AC heated, the AC cooled to room temperature. Then, the MAC was refluxed 3 times

* Corresponding Author: S M Anisuzzaman,
E-mail: anis_zaman@ums.edu.my

for 3 h to remove any inorganic impurities such as metal ions, on the surface. Lastly, the MAC was dried at 110°C for 24 h [15,17].

2.2 Fourier transform infrared spectroscopy (FTIR) analysis

After the impregnation of AC using H₃PO₄, changes in the functional group of both unmodified AC and MAC were compared and the spectra was recorded within 400 to 4000 cm⁻¹. The characterization of unmodified and MAC was done by using Fourier – transform infrared spectroscopy (FTIR) (Perkin Elmer).

2.3 Oil adsorption

The sorption of oil on the surface of water was conducted using methods from Nwadiogbu *et. al.*, [17]. 1 g of MAC was placed in a 250 ml beaker containing 5 g of crude oil which was collected from Sabah basin, Malaysia displaced in 100 ml of water at room temperature. The samples were left in the mixture for an approximation of 2 min with minimum agitation. The sorbents were removed from the beakers using sieve nets and the oil-loaded sorbents were then dried at 60°C for 30 min. The oil sorption capacity was calculated using equation 1:

$$\text{Oil sorption capacity } \left(\frac{g}{g}\right) = \frac{(S_{st}-S_o)}{S_o} \quad (1)$$

where, S_o is the initial mass of the dry sorbent, S_{st} is the mass of the sorbent with oil at the end of the sorption test.

The amount of crude oil adsorbed (q_e) was calculated using the equation 2:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

where, C_o is the initial concentration (mg/l); C_e is the equilibrium oil concentration (mg/l); V is the volume of the solution (l); W is the mass of adsorbent (g)

2.4 Adsorption equilibrium study

Adsorption isotherm is the relationship between adsorption capacity and concentration of the remaining adsorbent at constant temperature. Langmuir and Freundlich equations were used as mathematical expressions to describe the isotherm of the adsorption [120 -22]. To analyse the rate and mechanism of oil sorption toward AC and MAC, kinetic models were applied as Lagergren pseudo-first order and pseudo-second order [17,23].

3. Results and Discussion

3.1 Fourier transform infrared spectroscopy (FTIR) analysis

Figure 1 (a,b) shows the FTIR spectra for both unmodified AC and MAC. As observed, there is less difference in the peaks occurred in around 2500-2000 cm⁻¹ and strong peaks are detected in MAC around 1500-1000 cm⁻¹. The AC and MAC shows a similarity in a strong peak at 2326.54 and 2324.68 cm⁻¹ respectively which indicates that a C≡C exists in both of them caused by the stretching vibrations of the alkyne groups. Other than that, a peak was detected at 1300-1200 cm⁻¹ in the MAC graph which indicates the C-O-C group stretches in alcohols, phenols, esters, ethers and acids. At 980-950 cm⁻¹ of the MAC graph, P-O-C carbon peak stretches towards the area. This is due to the acid phosphates formation in the samples which were modified using H₃PO₄ [20]. Meanwhile, in both unmodified AC and MAC graphs, peaks that arise in the range of 800 – 700 cm⁻¹ may be caused by the existence of C-H [24].

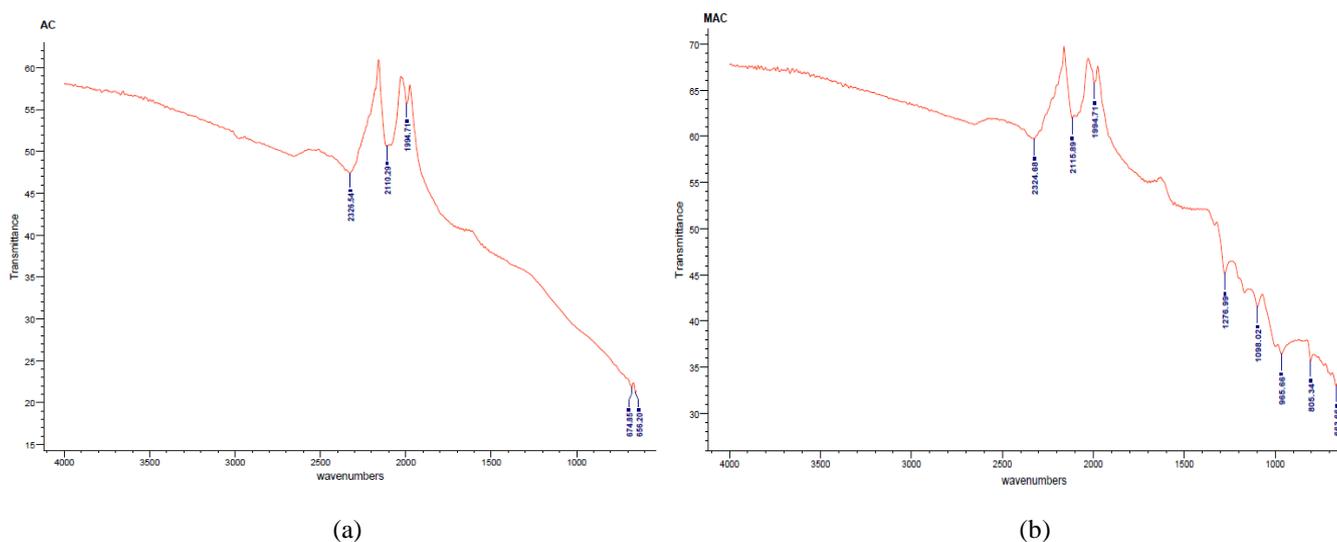


Figure 1. FTIR spectra of (a) unmodified AC (b) MAC

3.2 Effect of sorbent dosage towards oil sorption capacity

Table 1 shows the effect of oil sorption capacity towards the sorbent dosage. It can be observed that MAC has higher sorption capacity than AC at any given sorbent dosage. A trend was observed with an increase in sorbent dosage but a decrease in adsorption capacity. It was found that sorption capacity decreased 83.8% for unmodified AC and 83.2% for MAC with an increase in sorbent dosages.

Table 1. Effects of sorbent dosage towards oil sorption capacity on unmodified AC and MAC

Sorbent dosage, g	Oil sorption capacity, g/g	
	Unmodified AC	MAC
0.1	25.61	29.10
0.3	9.44	10.08
0.5	5.43	6.26
0.7	4.15	4.87

The decrease in sorption capacity may be due to the overlapping of AC, which results in a decrease in effective surface area for the adsorption process. It can be observed that the oil sorption capacity decreases with increasing sorbent dosage. It was also observed that after a certain dosage, at 0.5 g to 0.7 g, the efficiency of adsorption did not increase significantly. Therefore, the optimum amount of AC and MAC is 0.1g for both and was kept constant for the next adsorption experiments [25].

3.3 Effect of temperature towards oil sorption capacity

Table 2 shows the effect of temperatures towards the oil sorption capacity on both unmodified AC and MAC. Contact time and sorbent dosages were kept constant throughout the experiment meanwhile the temperatures were manipulated. It can be observed that MAC has higher oil sorption capacity than AC at any selected temperature.

Table 2. Effects of temperature towards the oil sorption capacity on unmodified AC and MAC

Temperature, °C	Oil sorption capacity, g/g	
	Unmodified AC	MAC
25	25.61	29.10
30	25.68	27.90
35	26.05	28.03
40	25.50	28.07

MAC has higher oil sorption capacity than AC due to the modification of H_3PO_4 . The modification enhances the porosity structure and sizes of the pores which consequently provides a better adsorption than unmodified AC [15]. The highest oil sorption capacity recorded for MAC was at a temperature of 25°C. The inconsistencies of the oil sorption capacity for both AC and MAC from 30°C to 40°C may be due to the increasing temperature which causes the oil to be very light which then leads to release of the oil from pores again [26]. According to El-Din *et al.*, [26], with the increase in temperature, the Brownian motion of oil particles is accelerated and increased proportional to the temperature.

3.4 Effect of contact time towards the oil sorption capacity

Table 3. shows the oil sorption capacity against contact time on unmodified AC and MAC.

The sorption capacity increases as time increases from 2 to 8 min. It was found that sorption capacity for unmodified AC was increased 5.8% and 12.4% for MAC with an increase in contact time. As observed, the maximum oil sorption capacity was recorded on the 8 min of contact time with a result of 27.10 g/g for AC and 32.71 g/g for MAC.

Table 3. Effect of contact time towards the oil sorption capacity on unmodified AC and MAC

Contact time, min	Oil sorption capacity, g/g	
	Unmodified AC	MAC
2	25.61	29.10
4	26.15	31.02
6	27.00	31.90
8	27.10	32.71

Figure 2 shows the regression plot of oil sorption capacity against contact time for both unmodified AC and MAC. According to the regression equation, for every 1 min increase in time, the oil sorption capacity for AC increases by 1%. Meanwhile, for the MAC, the oil sorption capacity increases by 2%. These results show that contact time does affect the oil sorption capacity of the modified and unmodified activated carbon.

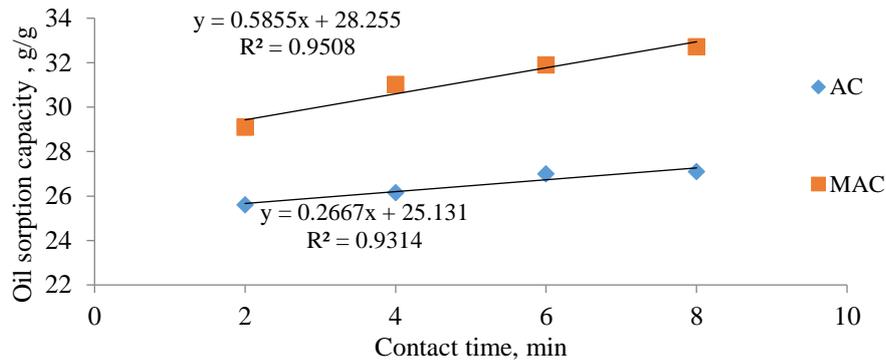


Figure 2. Regression plot of oil sorption capacity against contact time for both AC and MAC

3.5 Adsorption kinetic study

Figures 3 and 4 show the pseudo-first order and pseudo-second order kinetics for unmodified AC and MAC

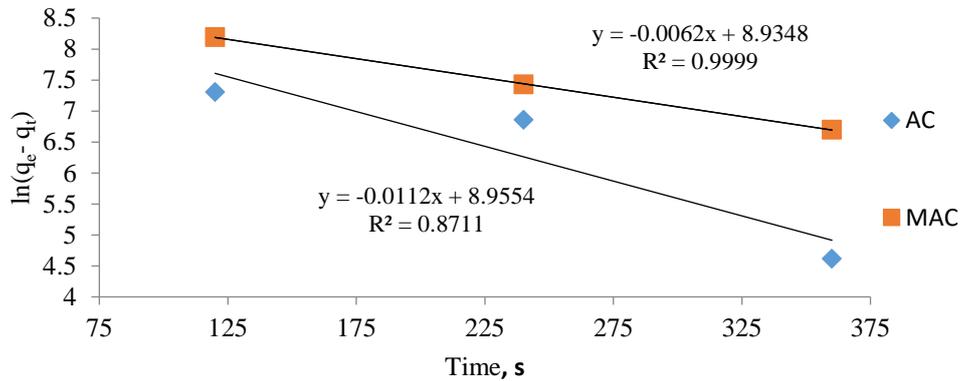


Figure 3. Pseudo-first order kinetics for unmodified AC and MAC

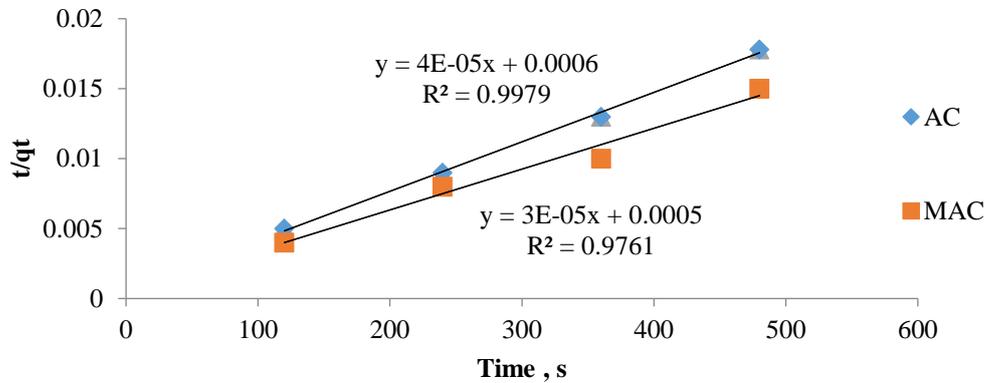


Figure 4. Pseudo-second order kinetics for AC and MAC

Table 4 shows the kinetic parameters data calculated from the Figures 3 and 4 for pseudo-first order and pseudo-second order models.

Table 4. Pseudo-first order and pseudo-second order parameters for AC and MAC

Kinetic Models	AC	MAC
Pseudo-first order:		
k_1 (s ⁻¹)	-0.0112	-0.0062
R^2	0.8711	0.9999
Pseudo-second order:		
k_2 (s ⁻¹)	4×10^{-4}	1.3×10^{-6}
R^2	0.9979	0.9761

Based on the result in Table 4, both kinetic models showed a good fit of kinetic to the data. However, for MAC the comparison between the first and second order, pseudo-first order expression provided an excellent fit to the experimental data as the regression coefficient (R^2) value was closer to 1 than pseudo-second order expression. The regression

coefficient (R^2) of MAC for the pseudo-first order was 0.9999. On the other hand, the regression coefficient (R^2) for pseudo-second order was 0.9761 for MAC. Hence, the pseudo-first order was chosen for the best kinetic model to express the sorption of crude oil on MAC [28].

3.6 Adsorption equilibrium study

Sorption isotherms are the basic representation of the relationship between amounts of adsorbate removed from the liquid phase and the mass of adsorbent at a constant temperature [19].

Figure 5 shows the Langmuir isotherm for AC and MAC.

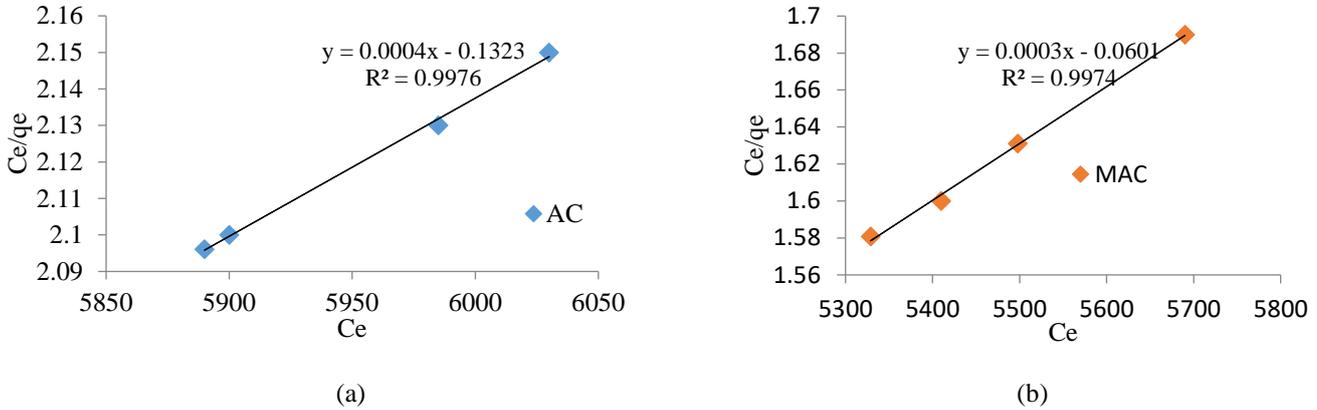


Figure 5. Langmuir isotherm (a) for AC (b) for MAC

Error! Reference source not found.5 shows the Langmuir isotherm constants obtained from this study.

Table 5. Langmuir isotherm models of AC and MAC

Isotherm models	AC	MAC
Langmuir:		
q_0	2500	3333
b	3.02×10^{-3}	4.99×10^{-3}
R_L	0.0367	0.0225
R^2	0.9976	0.9974

As shown in Table 5, the regression coefficient (R^2) was 0.9974 for MAC and 0.9976 for AC, which indicates the monolayer adsorption isotherm can provide a proficient fit for the sorption of crude oil onto the AC. The main concern of Langmuir isotherm is the separation factor (R_L). As mentioned by Nwadiogbu *et al.*, [19] that the sorption is considered irreversible if the $R_L = 0$, favourable if the value of R_L ranges from 0 to 1, linear if $R_L = 1$, or unfavourable if the R_L value is more than 1. From the experimental data it was found that the R_L for both AC and MAC are 0.0367 and 0.0225 respectively, which indicates that the sorption of crude oil on both AC and MAC is favourable. Figure 6 shows the Freundlich isotherm for AC and MAC.

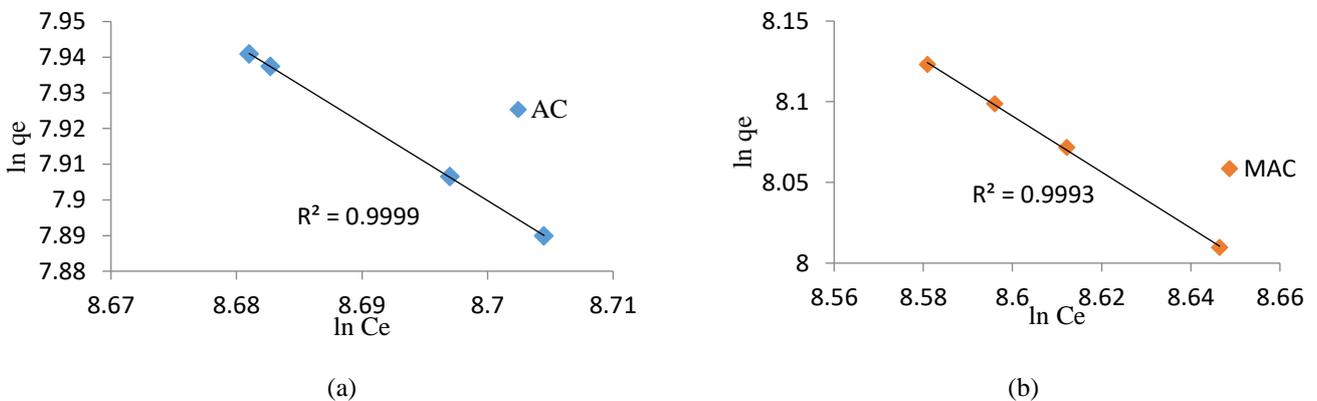


Figure 6. Freundlich isotherm (a) for AC (b) for MAC.

Error! Reference source not found.6 shows the Freundlich isotherm constants obtained from this study.

Table 6. Freundlich isotherm models of AC and MAC

Isotherm models	AC	MAC
Freundlich:		
K_F	4.3084×10^{11}	9.7839×10^9
$1/n$	2.1722	1.7341
R^2	0.9999	0.9993

The value of the regression coefficient in the Freundlich isotherm for AC and AC was 0.9999 and 0.9993 respectively. This isotherm obtained was higher than Langmuir model. Therefore, the result indicates that Freundlich is the most suitable model for describing the sorption equilibrium of crude oil on AC and MAC [28].

4. Conclusion

The FTIR spectra indicate that the number of pores found on the surface of MAC is higher than AC. The optimum sorbent dosage for both AC and MAC was found to be 0.1 g. Meanwhile for temperature effect, it was found that with higher temperature, oil sorption capacity decreases for both AC and MAC. As for the contact time effect, the maximum oil sorption capacity was recorded on the 8 min of contact time with a result of 27.10 g/g for AC and 32.71 g/g for MAC. For the kinetic study, pseudo-first order was chosen for the best kinetic model to express the sorption of crude oil on MAC as it shows the R^2 value closest to 1. Meanwhile, for the adsorption isotherm, the result indicates that Freundlich is the most suitable model for describing the sorption equilibrium of crude oil on AC and MAC. In this study, the equilibrium data was obtained from the batch test which may not be suitable for the real application. Hence, further study is recommended to simulate the performance of MAC to clean-up crude oil spills from water surface, using Aspen Adsorption® based on data from batch experiments.

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Characterization and Analysis of Bioethanol Blended Fuel as an Alternative Transportation Fuel in Bangladesh

Laila Hossain, Samavi Farnush Bint-E-Naser, Mohidus Samad Khan*

*Department of Chemical Engineering, Bangladesh University of Engineering & Technology,
Dhaka-1000, Bangladesh*

Received: 15 February 2022; Accepted: 1 December 2022; Published: 30 April 2023

Abstract: In Bangladesh, the demand for petroleum products has been increasing over the years. Transportation sector is the principal consumer of petroleum products in this country. At present, diesel, petrol (80 RON gasoline), and octane (95 RON gasoline) are the petroleum-based transportation fuels commonly used in Bangladesh. Domestically produced petrol from crude oil and condensate is adequate to meet the local demand; however, Bangladesh has to import most of the octane. Besides, petroleum derivatives contribute significantly to the GHG emission load of the country. To ensure energy security, to reduce expenditure of foreign currency and dependence on foreign supply, and to secure the environment, Bangladesh is currently exploring renewable energy sources. Bioethanol produced from biomass can be a potential eco-friendly alternative energy source for Bangladesh. Although Bangladesh does not commercially produce bioethanol till date, there have been few initiatives at the private sector in this regard. Therefore, it is important to understand the feasibility of using bioethanol and bioethanol blends as alternative transportation fuel in Bangladesh. In this study, key fuel properties (specific & API gravity, RVP, viscosity, calorific value, sulfur content, copper corrosion, water & bottom sediment, water content, carbon residue, and ASTM distillation), and pollutant emission characteristics (carbon monoxide, carbon dioxide and hydrocarbon emission) of bioethanol blend petrol and octane were analyzed at various blending ratios. Physicochemical properties of bioethanol blended petrol and octane were found up to standard. Results show that, when blended with petrol and octane at low ratios, locally produced bioethanol causes less than 1 psi increase in RVP, around 10 percent decrease in calorific value, up to 5 percent reduction in sulfur content, and warrants minimum or no modification of conventional spark ignition engines. Experimental data from emission analysis indicates that using bioethanol blends is favorable from environmental viewpoint due to lesser pollutant emission. Impact on food cycle analysis shows that producing bioethanol locally, to replace up to 10 percent of the combined use of petrol and octane, will have minimum impact on the food security of the country. This study will provide the feasibility analysis of local production of bioethanol and the baseline properties of bioethanol blends as alternative transportation fuel.

Keywords: Bioethanol, transportation, fuel characteristics, economy, environment, food security.

1. Introduction

Globally the demand for energy is gradually increasing because of the limited reserve of fossil fuels, their unstable market price and detrimental impact on the environment and human life, the use of renewable energy has been gaining ground. With significant agricultural and industrial development, the demand for energy in Bangladesh is also growing consistently. In Bangladesh, transportation sector is one of the primary consumers of energy, accounting for more than half of the total demand for petroleum products in the country [1]. Currently, Compressed Natural Gas (CNG) along with petroleum derivatives, namely, diesel, petrol (80 RON gasoline), and octane (95 RON gasoline), are used as transportation fuels in Bangladesh. Even though approximately 300,000 motor-driven vehicles are using CNG as fuel in this country [2], the demand for petroleum-based transportation fuels is still growing [3]. Moreover, to preserve the limited reserve of natural gas in the country, the government has already restricted access to CNG by limiting the dispensing hours and increasing the price [4]. Such restrictions coupled with the increasing number of vehicles in the country will inevitably cause the demand for transportation fuel to rise in the upcoming years. On the other hand, exhaust emission from the rapid growth of transportation vehicles is adversely affecting the mass population. Vehicular air pollution is a major cause of respiratory distress in the urban areas of Bangladesh [5]. Therefore, for sustainable economic growth, it is essential for Bangladesh to look for renewable, alternative fuel sources to meet the growing demand for transportation fuel.

Considering the above-mentioned issues, it has become imperative for Bangladesh to explore locally available renewable energy sources to provide clean fuel [6]. Bioethanol can be a potential renewable energy source to be used either as a fuel or as a gasoline enhancer in Bangladesh. Any biomass containing sugar can be used to produce bioethanol through fermentation. Being an agricultural country, Bangladesh produces a large amount of corn and broken rice, a portion of which can easily be used as raw material for bioethanol production. Recognizing the potential, initiatives have recently been taken in the private sector to produce bioethanol from broken rice and maize.

Bioethanol, when used as a gasoline additive, increases the octane number of gasoline and improves engine performance [7,8,9]. Plants and biomass, the raw materials of bioethanol, consumes carbon dioxide produced during the combustion of bioethanol, hence, bioethanol is carbon neutral. Several studies have shown that sugarcane-based ethanol may reduce GHG emissions up to 90 percent [10]. Moreover, bioethanol, unlike gasoline, is an oxygenated fuel that contains 35 percent oxygen, which reduces particulate matter, carbon monoxide (CO) and NO_x emission [11]. Compared to common gasoline additives, such as MTBE (Methyl Tertiary Butyl Ether) and benzene, bioethanol has greater octane booster properties [12]. The auto-ignition temperature and flash point of alcohol are higher than those of gasoline, which makes

* Corresponding Author: Mohidus Samad Khan,
E-mail: mohid@che.buet.ac.bd

it safer for transportation and storage [13]. Furthermore, the latent heat of evaporation of alcohol is 3–5 times higher than that of gasoline, which makes the temperature of the intake manifold lower, and increases the volumetric efficiency [14]. Using bioethanol as a gasoline supplement has numerous advantages; however, one of the major concerns about commercial production of bioethanol is the potential impact on food security. Bioethanol production process converts only the starch content of the raw material while the protein and other contents of raw materials remain the same. Hence, the by-product of the process, dry distillers grain solubles (DDGS), containing a high amount of protein, can be used as poultry and cattle feed, which is the main use of broken rice and other raw materials used for bioethanol production in Bangladesh. The cost of production and consequently, the price of bioethanol is currently higher than petrol or octane in Bangladesh. Nevertheless, the price of petroleum products is often fluctuating. Moreover, using advanced technology in bioethanol production process is bringing down the cost of production while increasing yield [15,16,17,18]. Thus, in the coming future, replacing a percentage of the current use of petrol and octane can reduce dependence on import and save foreign exchange, and thereby, lead to a more stable economy for Bangladesh [6]. Also, domestic bioethanol production will create job opportunities. According to the Renewable Fuel Association, ethanol industry jobs have proven to be stable, well paid, fulfilling, and safe [19].

It is important to evaluate the physicochemical properties of locally produced bioethanol, bioethanol blends and the potential impact on local economy and food security. In this study, key fuel properties and pollutant emission characteristics of bioethanol blend petrol and octane, and the protein content of DDGS were analyzed. Current fossil fuel consumption along with their negative effects has been critically discussed to address the necessity of bioethanol blends as transportation fuel in Bangladesh. Economic aspects attributed to the annual consumption of petrol and octane, and possible savings resulting from replacing a fraction of the fossil fuel by bioethanol has been assessed as well. Availability of raw materials required for producing bioethanol locally and possible impact on food economy have also been analyzed. Overall, this study will give a comprehensive idea about the feasibility of using bioethanol blend fuels as an alternative transportation fuel in Bangladesh.

2. Material and Methods

In this study, key fuel properties of bioethanol, petrol, and octane samples along with bioethanol blend petrol and octane samples containing 5, 10, 15 and 20 percent bioethanol were assessed. The pollutant emission of a Spark Ignition (SI) engine was also investigated using petrol, octane, and bioethanol blend petrol and octane samples containing 5 and 10 percent bioethanol. The protein content of broken rice, maize, and DDGS was determined to evaluate the use of DDGS as animal feed as well.

2.1 Sample Collection and Preparation

Fuel-grade bioethanol sample was collected from Sunypun Organics Limited, Bangladesh. The collected bioethanol sample was produced from multi-feedstock, which was converted to monomeric sugars via enzymatic hydrolysis. The sugars were fermented using yeast to produce bioethanol. The produced bioethanol was purified in a multi-pressure distillation column with integrated evaporator operating under vacuum at low temperature and then dehydrated to obtain the final product (Figure 1).

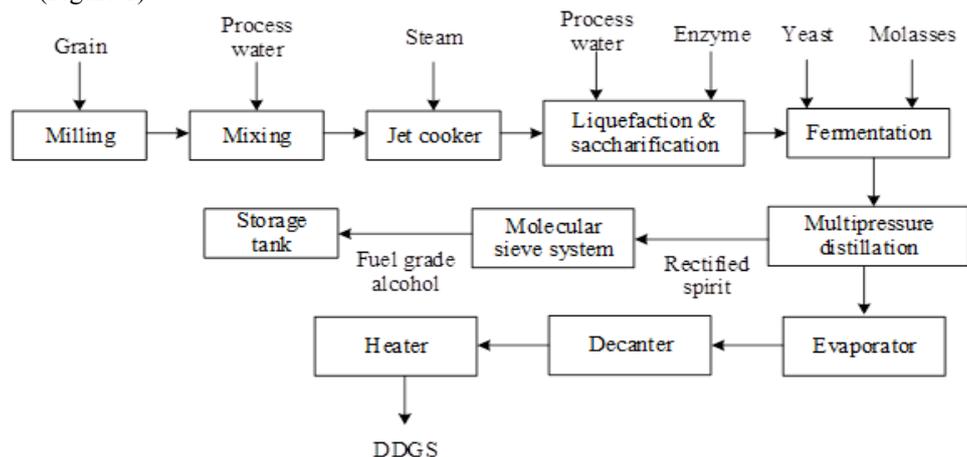


Figure 1: Simplified block diagram of bioethanol production process.

Petrol and octane were purchased from local fuel station (Nilkhet, Dhaka). The bioethanolblend petrol and octane samples containing 5, 10, 15 and 20 percent bioethanol were prepared in the laboratory using the collected bioethanol sample, petrol, and octane. For further discussion, the samples will be referred to by their individual sample ID (Table 1).

Table 1: Sample identification

Sample	Sample ID
Bioethanol	E100
Petrol	P-E0
5 per cent bioethanol blended with petrol	P-E5
10 per cent bioethanol blended with petrol	P-E10
15 per cent bioethanol blended with petrol	P-E15
20 per cent bioethanol blended with petrol	P-E20
Octane	O-E0
5 per cent bioethanol blended with octane	O-E5
10 per cent bioethanol blended with octane	O-E10
15 per cent bioethanol blended with octane	O-E15
20 per cent bioethanol blended with octane	O-E20

2.2 Methodology

2.2.1 Fuel properties

For this study, several fuel properties were tested according to ASTM specification. These test methods are listed in Table 2.

Table 2: List of test methods.

Parameter tested	ASTM test method
Specific gravity	ASTM D 1298-99
Reid vapor pressure	ASTM D 323-99a
Viscosity	ASTM D 88-94
Calorific value	ASTM D 2014-96
Sulfur content	ASTM D 3177-89
Copper corrosion	ASTM D 130-04
Water & bottom sedimentation	ASTM D 1796-97
Water content	ASTM D 95-70
ASTM distillation	ASTM D 86-04b

Carbon residue of all samples was tested by gravimetric method. The water content of bioethanol was additionally calculated using the specific gravity of the sample, which was measured by hygrometer, and data from Table 2-110 of section 2 from Perry's Chemical Engineers' Handbook [20]. The water in the samples containing various concentrations of bioethanol was calculated using material balance.

Each test was carried out minimum three times ($n=3$) and the average results were used for further analysis.

2.2.2 Emission analysis

Pollutant emission upon combustion, namely, carbon monoxide (CO), carbon dioxide (CO₂), and hydrocarbon (HC) emissions, was analyzed for the P-E0, P-E5, P-E10, O-E0, O-E5, and O-E10 blends. Two separate engines of the same model (1MZ-FE, 1496 cc, manufacturer: Toyota Motor Corporation) were used for the bioethanol blend petrol and octane samples. Both engines were run at two different engine speeds: 750 rpm and 3000 rpm. The exhaust gas samples were analyzed with an emission analyzer (Analizzatore gas model 810) to detect CO, CO₂ and HC levels.

2.2.3 Protein Analysis

The raw materials (corn and broken rice) and the by-product (DDGS) of the bioethanol production process were analyzed by Kjeldahl method [21] to determine their individual protein contents.

3. Results

3.1 Fuel Properties

The key fuel properties of bioethanol blend petrol and octane samples have been summarized in Tables 3, 4 and 5. Table 3 shows the variation of specific gravity, API gravity, Reid Vapor Pressure (RVP), viscosity, calorific value and sulfur content as a function of blend rate. Table 4 contains results for copper strip corrosion test and carbon residue content for various blends. Table 5 represents the water content of all samples obtained according to three separate methods: ASTM D 1796-97, ASTM D 95-70 (toluene distillation), and calculated values using specific gravity data recorded at 20°C. During the ASTM distillation test, Initial Boiling Point (IBP), Final Boiling Point (FBP), percent loss and total recovery data were recorded, which are shown in Table 6.

Table 3: Experimental results of specific gravity, API gravity, vapor pressure, viscosity, calorific value, and sulfur content.

Sample ID	Specific gravity at 20°C	API Gravity	RVP (kPa at 37.8°C)	Viscosity (cSt)	Calorific value (MJ/kg)	Sulfur content (wt%)
E100	0.785	49.0	14.25	1.03	27.33	0.036
P-E0	0.757	56.5	45.75	0.55	40.72	0.0480
P-E5	0.761	56.0	43	0.56	40.44	0.0474
P-E10	0.762	55.5	43	0.57	39.38	0.0467
P-E15	0.764	55.0	50	0.57	38.69	0.0461
P-E20	0.764	54.8	45.5	0.59	37.11	0.0454
O-E0	0.777	51.8	50	0.55	40.59	0.0500
O-E5	0.781	51.5	48	0.57	40.07	0.0493
O-E10	0.784	50.8	51.5	0.58	40.08	0.0486
O-E15	0.787	49.3	45	0.58	38.34	0.0478
O-E20	0.788	49.0	45.5	0.61	36.06	0.0471

Table 4: Experimental results of copper strip corrosion and carbon residue content.

Sample ID	Copper strip corrosion		Carbon residue (wt%)
	50°C	100°C	
E100	1a	1a	0.011
P-E0	1a	1a	0.014
P-E5	1a	1a	0.023
P-E10	1a	3a	0.008
P-E15	1a	3a	0.024
P-E20	1a	3a	0.031
O-E0	1a	1a	0.036
O-E5	1a	1a	0.038
O-E10	1a	3a	0.008
O-E15	1a	3a	0.004
O-E20	1a	3a	0.007

Table 5: Experimental results of water content

Sample ID	Water content (%)		
	ASTM D 1796	Toluene distillation	Calculated (using specific gravity & material balance)
E100	Nil	Nil	0.01
P-E0	Nil	Nil	0.01
P-E5	Nil	Nil	0.01
P-E10	Nil	Nil	0.01
P-E15	Nil	Nil	0.01
P-E20	Nil	Nil	0.01
O-E0	Nil	Nil	0.01
O-E5	Nil	Nil	0.01
O-E10	Nil	Nil	0.01
O-E15	Nil	Nil	0.01
O-E20	Nil	Nil	0.01

Table 6: Experimental results of ASTM Distillation of petrol, octane and bioethanol blend fuel.

Sample ID	ASTM distillation			
	IBP (°C)	FBP (°C)	Percent loss (%)	Total recovery (%)
E100	81.0	83.0	0.50	99.50
P-E0	54.2	266.4	0.95	99.05
P-E5	60.3	286.5	0.95	99.05
P-E10	49.9	239.8	2.07	97.93
P-E15	49.9	187.9	2.05	97.95
P-E20	45.0	200.0	2.50	97.50
O-E0	46.2	224.4	2.77	97.23
O-E5	48.9	223.9	2.90	97.10
O-E10	48.25	248.41	2.76	97.24
O-E15	48.92	191.9	2.47	97.53
O-E20	52.0	204.0	3.0	97.0

3.2 Emission Analysis

Table 7 contains CO, CO₂ and HC emissions in the exhaust gas from an SI engine for the following samples: petrol, octane, and bioethanol blend petrol and octane samples containing 5 and 10 percent bioethanol.

Table 7: Experimental results of CO, CO₂ and HC emission.

Sample ID	CO emission (%)		CO ₂ emission (%)		HC emission (%)	
	750 rpm	3000 rpm	750 rpm	3000 rpm	750 rpm	3000 rpm
P-E0	0.01	0.04	13.3	13.3	3	8
P-E5	0.01	0.02	13.2	13.3	2	1
P-E10	0.01	0.01	13	13	3	1
O-E0	0.02	0.06	13.5	13.4	6	12
O-E5	0.01	0.01	13.5	13.4	5	1
O-E10	0.01	0.01	13.5	13.4	1	1

3.3 Protein Analysis

The protein and moisture content of both the raw materials (corn, broken rice) and the by-product (DDGS) of the bioethanol production process are given in Table 8.

Table 8: Protein and moisture content of corn, broken rice and DDGS.

Sample	Protein content (wt%)	Moisture content (wt%)
Broken rice	7.08	8.32
Maize	7.88	9.69
DDGS	23.67	8.01

4. Discussions

4.1 Fuel Properties

4.1.1 Specific Gravity

Specific gravity is an indicator of fuel economy, power, deposits, wear, and exhaust smoke [22]. Generally, an increase in density increases the overall performance of engines [23]. Bioethanol has a slightly higher molecular weight than both petrol and octane, and consequently, addition of bioethanol caused increase in the specific gravity of the blends (up to 2.3 percent for bioethanol blend petrol and 1.4 percent for bioethanol blend octane), as demonstrated in Figure 2.

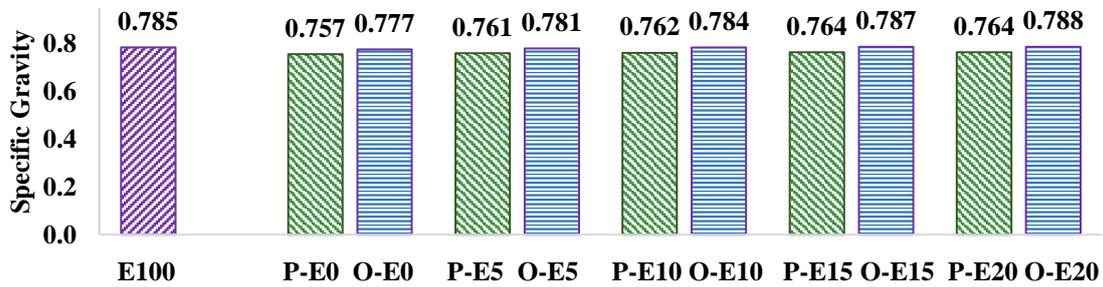


Figure 2: Effect of blending bioethanol on the specific gravity of petrol and octane.

4.1.2 API Gravity

The American Petroleum Institute gravity, or API gravity, is used to compare densities of petroleum liquids to magnify small differences in density. Figure 3 shows the effect of blending bioethanol on the API gravity of petrol and octane. For both bioethanol blend petrol and octane, API gravity decreased with increasing percentage of bioethanol; up to 3 percent and 5.4 percent reductions were observed for P-E20 and O-E20 respectively, which calls for no special modification of the traditional combustion engines [24].

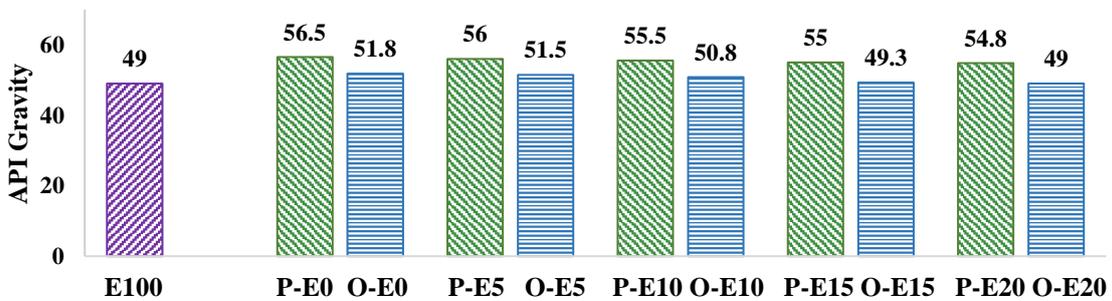


Figure 3: Effect of blending bioethanol on the API gravity of petrol and octane.

4.1.3 Reid Vapor Pressure

RVP is frequently used as an indication of the volatility of liquid hydrocarbons [25]. Petrol and octane are manufactured as liquids but they are consumed in the vapor phase. Consequently, their volatility must be high enough to assure acceptable engine start-up, warm-up, acceleration and throttle-response under normal driving conditions. On the other

hand, the maximum volatility of petrol or octane must be restricted to avoid vapor lock, vaporization losses, unsafe storage and handling, and evaporative emissions of smog-forming hydrocarbons, which are undesirable from the environmental viewpoint.

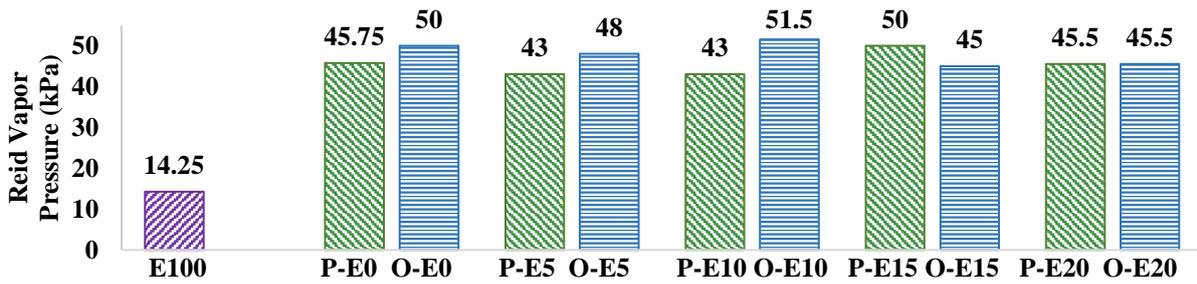


Figure 4: Effect of blending bioethanol on the Reid vapor pressure of petrol and octane.

According to RFA guidelines, unless other more volatile blending components are being used, the addition of ethanol should not create a vapor pressure increase above 1.0 psi (6.89 kPa) in conventional gasoline [26]. The experimental measurements as demonstrated in Figure 4 shows that blending of bioethanol caused an increase in RVP lower than 6.89 kPa for all bioethanol blend petrol and octane samples. Among the bioethanol blend octane samples, the blend containing 10 percent bioethanol showed the highest RVP, which is similar to the findings of other research groups [27].

4.1.4 Viscosity

Viscosity affects heat generation in bearings, cylinders, and gear sets related to an oil's internal friction. It governs the sealing effect of oils and the rate of oil consumption, as well as determining the ease with which machines may be started or operated under varying temperature conditions, particularly in cold climates.

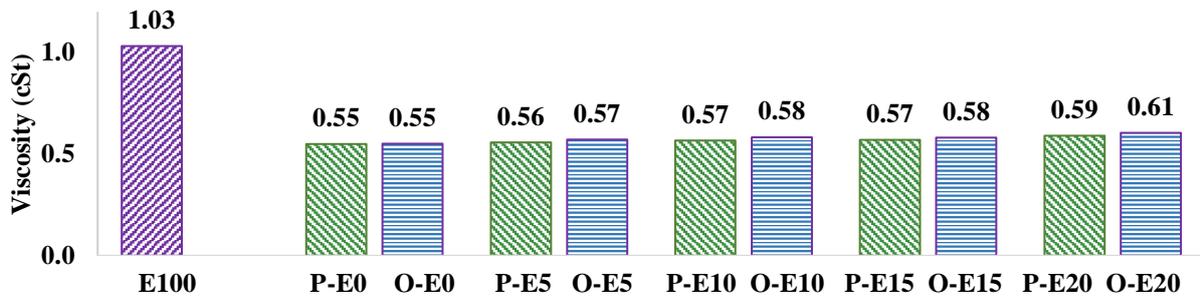


Figure 5: Effect of blending bioethanol on the viscosity of petrol and octane.

Figure 5 shows that blending of bioethanol up to 20 percent volume content caused a small increase in viscosity (maximum 7 percent increase and 10 percent increase for bioethanol blend petrol and octane samples were observed).

4.1.5 Gross Calorific Value

The Gross Calorific Value (GCV) is used to compute the total calorific content of fuel in order to determine if the fuel meets regulatory requirements for industrial fields. The combustion rate of a fuel is proportional to its calorific value.

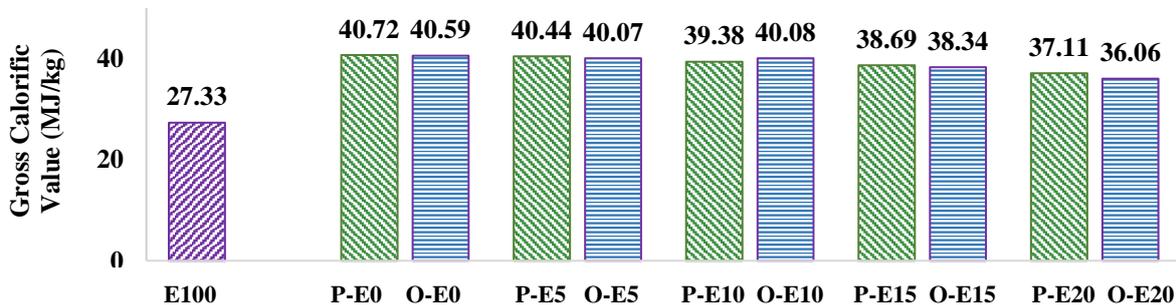


Figure 6: Effect of blending bioethanol on the gross calorific value of petrol and octane.

The GCV of bioethanol is lower than that of both petrol and octane, and accordingly, the GCV of the blends were found to be lower than the pure fuel samples; maximum 9% decrease for bioethanol blend petrol and 11% decrease for bioethanol blend octane (Figure 6) were observed. This indicates that to produce the same amount of energy, more bioethanol is needed than either petrol or octane. Generally, 1.5 gallons of fuel grade bioethanol has the same energy content as 1 gallon of petrol or octane [6]. Based on the results of this study, 1.45 gallons of bioethanol was found to have the same energy content as 1 gallon of gasoline. Since the locally produced bioethanol performed almost similar to fuel grade ethanol under test conditions, it is deemed suitable for use as a gasoline supplement.

4.1.6 Sulfur Content

Sulfur and its compounds are present in most of the petroleum products and lubricants. Sulfur in fuel is undesirable because it damages the engines through abrasive wear of the piston rings and cylindrical walls, and pollutes the environment by causing acid rain and particulate emission [29-31].

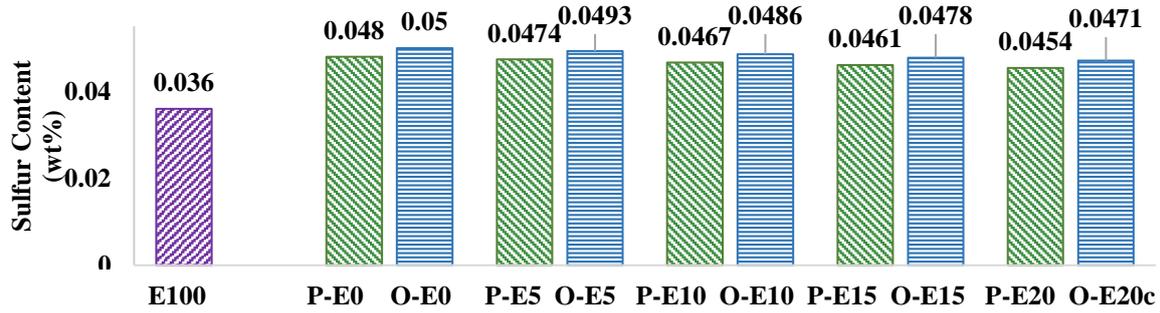


Figure 7: Effect of blending bioethanol on the sulfur content of petrol and octane.

From Figure 7, it is evident that blending of bioethanol resulted in a decreased amount of sulfur in the blends (up to 5 percent and 6 percent decrease for bioethanol petrol and octane respectively) since the sulfur content of bioethanol is lower than fossil fuels.

4.1.7 Copper Strip Corrosion

The copper strip corrosion test assesses the relative degree of corrosivity of a petroleum product. As recorded in Table 4, all samples under test showed the same degree of corrosivity, causing a slight tarnish (1a) in the color of the copper strip, at the prescribed test temperature (50°C according to ASTM 130-04). However, for the purpose of this study, additional tests were carried out at a higher temperature (100°C).

At the higher temperature, samples containing higher than 5 percent bioethanol caused a dark tarnish (3a) in the copper strip, representing a higher degree of corrosion. Therefore, additional protective measures, such as corrosion inhibitors, may be required to prevent corrosion of engine, fuel tank, and fuel transmission system etc., when fuel blends containing more than 5 percent bioethanol are used. In different developed countries including USA, Australia, and in several European countries, corrosion protective chemicals are used along with bioethanol blends containing more than 10 percent bioethanol [30,32,33].

4.1.8 Carbon Residue

The carbon residue value serves as an approximation of the tendency of petroleum products to form carbonaceous deposits under similar degradation conditions. Figure 8 shows the carbon residue of all samples, which were found to be sufficiently low.

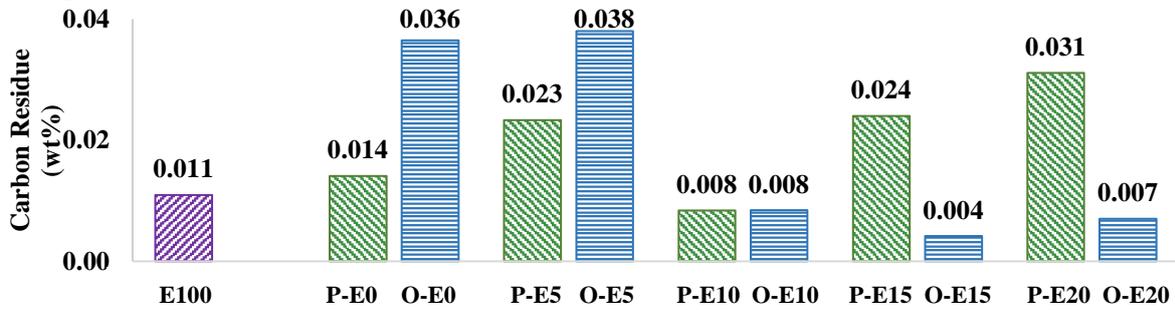


Figure 8: Effect of blending bioethanol on the carbon residue of petrol and octane.

4.1.9 Water Content

Determining the water content of fuels and biofuels is important for quality control, meeting trade specifications, protecting financial value, enhancing process optimization, and for taking necessary steps to reduce risks from corrosion, safety problems, and infrastructure damage [34]. The moisture content of petrol, octane, and bioethanol samples, tested according to ASTM D 1796-97 and ASTM D 95-62 (Toluene Distillation Method), were found to be below the detection limit of the equipment used for the tests (Table 5).

However, for the purpose of this study, the water content of all samples was also calculated as described in section 2.2.1. Since the collected petrol and octane samples were refined, it was assumed that those samples contained minimum amount of water (0.01 vol%). The water content of bioethanol calculated using specific gravity was also found to be 0.01 percent (vol%), and consequently, the water content of the blends, calculated using material balance, were found to be very low (Table 5).

4.1.10 ASTM Distillation

Figure 9 (a) and 9 (b) shows the effect of blending bioethanol on the distillation curves of petrol and octane respectively. For efficient combustion, the curve should be smooth. A fluctuating curve implies an oil that may give erratic operation due to non-uniform conditions. The curve also graphically shows the degree of spread between the initial boiling point and the end point, which is important in judging the ignition properties of oil.

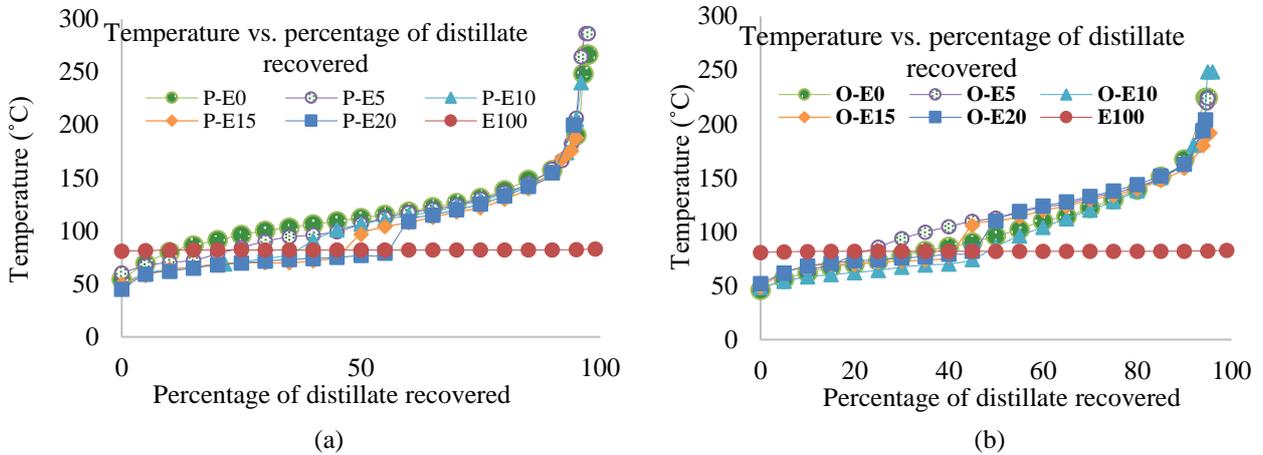


Figure 9: Effect of blending bioethanol on the boiling point of (a) petrol and (b) octane.

The boiling point range for petrol was found to be 54.2-266.4°C and for octane, it was 46.2-224.4°C (Figure 9). Bioethanol evaporated at an almost constant temperature of around 82°C. Petrol and octane are generally mixtures of hydrocarbons whereas bioethanol consists of almost pure C₂H₅OH. This contributed to the difference in the boiling behavior of pure bioethanol from those of pure petrol and octane.

The temperatures at which 10, 50, and 90 volume percent of petroleum products evaporate (T10, T50, and T90 respectively) are often used to characterize the volatility of gasoline [35]. As can be seen from Figure 9, blending bioethanol did not have significant effect on the T90 temperatures. For the bioethanol blend petrol samples, the T10 and T50 temperatures were lower than those of petrol were. For the bioethanol blend octane samples, the T10 temperatures remained almost the same. However, the T50 temperatures were slightly elevated for all bioethanol blend octane samples, except O-E10, for which the T10 was lower. It is evident from Figure 9 that addition of bioethanol generally lowered the boiling point, which indicates a lower tendency to form solid deposits during combustion [36].

4.2 Emission Analysis

Several studies on fuel tanks and fuel system components have examined and concluded that blending bioethanol with gasoline below 10 percent does not increase corrosion in everyday operation [37,38]. The experimental results of this study also support this. However, for fuel blends containing 10 percent bioethanol, corrosion inhibitor can be used to avoid any undesired corrosion [39,40,41]. Vehicles using higher bioethanol blend fuel may clog fuel filters, fuel pumps, and carburetors [42]. Hence, for this study, the exhaust gas from an SI engine using bioethanol blends, containing up to 10 percent alcohol as fuel, were collected at two different engine speed for analysis. The pollutant concentrations were generally higher at 3000 rpm due to shorter combustion time at a higher engine speed.

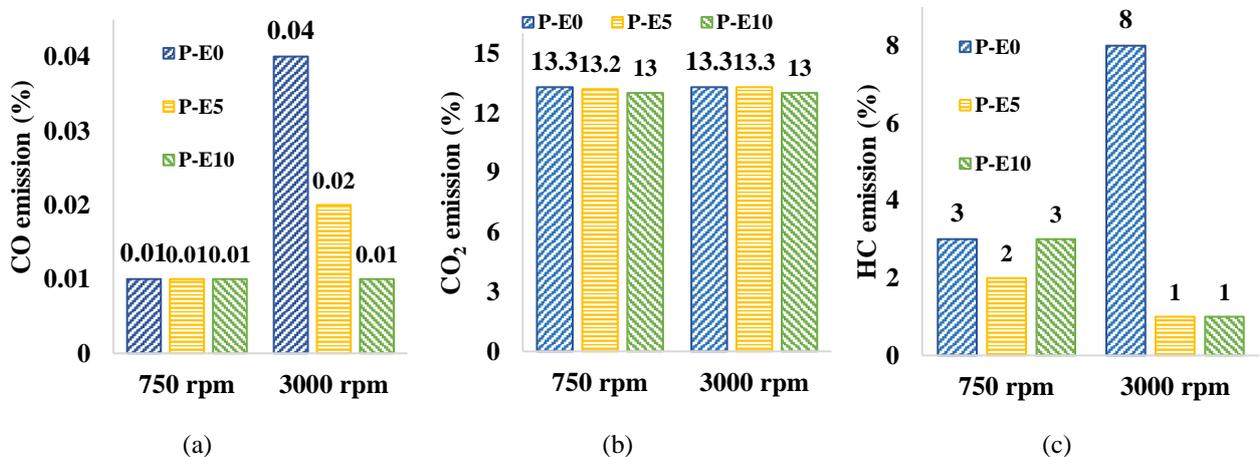


Figure 10: Effect of blending bioethanol on (a) CO (b) CO₂ and (c) HC emission by combustion of petrol.

As can be seen from Figures 10 (a) and 11 (a), for all samples, the addition of bioethanol had minimal or no effect on CO emission at the lower speed (750 rpm). At high engine speed (3000 rpm), CO emission was found to be lower for the bioethanol blends than pure petrol and octane. This indicates that the engine tends to operate in leaner and closer to stoichiometric burning conditions with increasing bioethanol content. Since the combustion process is more complete when it is closer to stoichiometric burning, CO emission decreases. Up to 75 percent and 83 percent reduction in CO emission were observed for the P-E10 and O-E10 blends respectively.

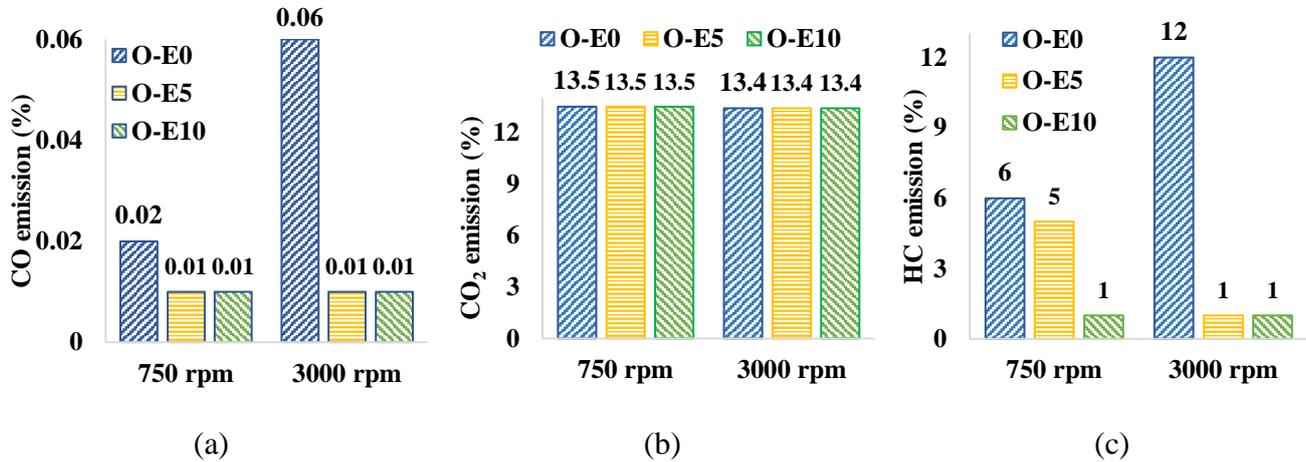


Figure 11: Effect of blending bioethanol on (a) CO (b) CO₂ and (c) HC emission by combustion of octane.

For all samples, CO₂ emission was not affected much by the presence of bioethanol at either speed (Figures 10 (b) and 11 (b)). However, bioethanol is considered carbon neutral, *i.e.* the amount of CO₂ released in the bioethanol production process would be consumed during photosynthesis of the crops and biomass. Therefore, the net annual CO₂ emission associated with the use of bioethanol blends is less than that associated with the use of petroleum fuels.

HC concentration in the exhaust was found to decrease with increasing bioethanol content (Figures 10 (c) and 11 (c)), which indicates that addition of bioethanol increases combustion efficiency. HC emission was reduced by as high as 88 percent and 92 percent for bioethanol blend petrol and octane samples respectively.

4.3 Use of By-Products: Dry Distillers Grain Solubles (DDGS)

Locally available materials, which can potentially be used to produce bioethanol (such as, broken rice, maize etc.), are currently used as animal feed in Bangladesh. Protein, fiber, ash content, fat, and lipid contents are few of the key ingredients of cattle, poultry and fish feeds [43,44,45,46]. Milled rice and maize contains 70-75 percent and 60-65 percent (weight basis) starch respectively [47]. Bioethanol production process converts the starch content of these grains to sugar through enzymatic reactions followed by fermentation, while the protein content remains almost unchanged, and is accumulated in the major byproduct of the process, DDGS. About 320 kg of DDGS can be recovered from 1 ton of grain (broken rice or maize) (ref: Moji Engineering Systems Ltd. and Sunypun Organics Ltd.). To assess the feasibility of using DDGS as alternative animal feed, the protein contents of broken rice, maize and DDGS were experimentally determined, and are shown in Figure 12.

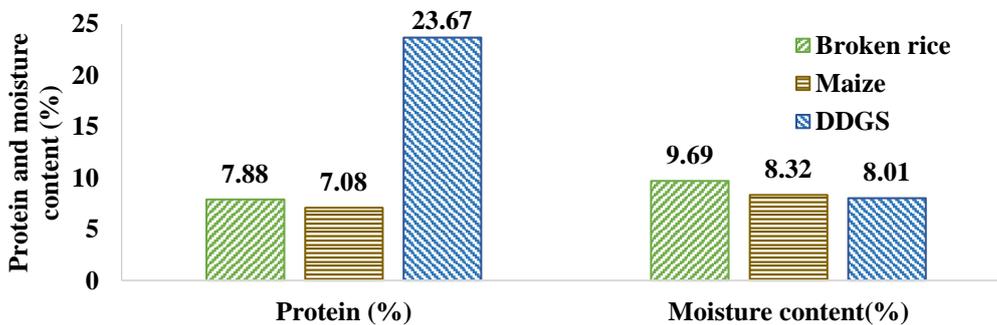


Figure 12: Protein content of corn, broken rice, and DDGS.

In Bangladesh, protein content in cattle feed and animal feed varies from 12 percent to 22 percent (Table 9). Protein content of DDGS was found to be around 24 percent, and therefore, DDGS is suitable for use as animal feed in the country. Table 9 compares the key nutritional requirements of fish feed, poultry feed, and cattle feed with the nutritional content of DDGS. DDGS contains non-fermentable solids from the grain, and it has high energy, high protein content (up to 30 percent), crude fiber (5-14 percent), crude fat (3 to 12 percent), ash (4 to 6 percent), minerals (>2.5 percent), (neutral/acid) detergent fibers, and moisture [48,49], which make it a useful additive or supplement for cattle, poultry and fish feeds [50].

Table 9: Key nutritional composition of fish feed, poultry feed and cattle feed [4,44,48,45,46]

Nutritional Parameters	Cattle Feed	Poultry Feed	Fish Feed	DDGS
Protein (wt %)	12-19	18-22	45-70	~ 30
Fiber (wt %)	17-22	7-20	-	5-14
Ether Extract (wt %)	3-4	5-9	-	~2.5
Fat and Lipid (wt %)	3-4	4-6	9-10	3-12
Ash (wt %)	-	6-11	10-12	4-6
Others	Others contain minerals (calcium, phosphorus, magnesium, sulfur, sodium, chlorine, manganese, copper, zinc, iron, cobalt, iodine, vitamins, etc.), carbohydrates, moisture, etc.			

5. Feasibility of Bioethanol Production Plant in Bangladesh

5.1. Global Scenario in Fuel Ethanol Production

In Brazil, as of 1984, approximately 7.9 million tons of ethanol was produced by fermentation of sugarcane sucrose, and as a result, petroleum imports were reduced [51]. The USA is also substantially increasing its fuel alcohol production, originally because of the fluctuation of petroleum costs, and the subsequent need for developing alternative energy sources [51]. Currently, Brazil has more than 300 ethanol plants, producing more than 7000 million gallons per year and supplying 3 million cars with pure ethanol [52]. In the USA, there are more than 80 plants producing over 15,000 million gallons of ethanol per year. In the year 2016, China, India, and Canada produced 845, 225 and 436 million gallons of ethanol respectively [52]. In the same year, approximately 1400 million gallons of ethanol were produced in the European Union. Bangladesh has the opportunity to follow the global trend of ethanol production.

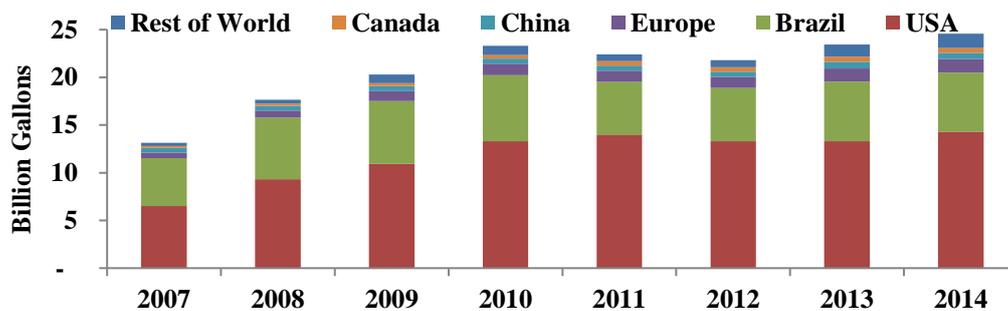


Figure 13: World Fuel Ethanol Production by country or region [52].

5.2 Current Energy Scenario: Prospect of Bioethanol in Bangladesh

In Bangladesh, the annual demand of petroleum products for the 2016-2017 fiscal year was about 5.88 million metric tons (MMT) [3]. This demand is met primarily by importing refined petroleum products, and to a lesser extent, by refining imported crude oil, which is processed along with domestic condensate and a small quantity of oil from local source: Haripur Gas Field at Sylhet, Bangladesh [53]. Considering the depletion of global fossil fuel reserves, the amount of foreign currency required to import the petroleum products, and the concern regarding environmental problems, it is essential for Bangladesh to look for alternative renewable fuel. Recently, Bangladesh Government has decided to use E5 (or, any other concentration permitted by the Government) as a transportation fuel. In this regard, the government has published a gazette about the setup of bioethanol plants on 12 December, 2017 [54].

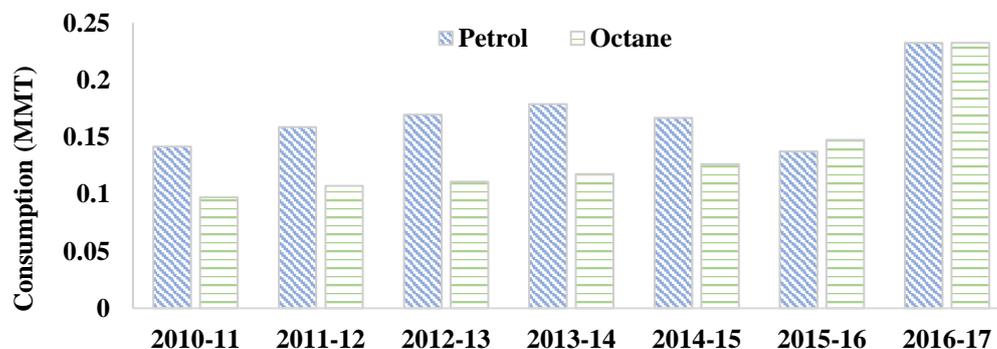


Figure 14: Annual consumption of petrol and octane in Bangladesh (in last seven fiscal years) [1]

In the fiscal year 2016-17, 232,359 metric tons (MT) petrol and 186,911 MT octane were consumed in Bangladesh (Figure 14) [1]. Replacement of 10 percent of the current petrol and octane consumption using bioethanol will reduce the annual consumption of these petroleum products up to 30.73 million liters and 24.72 million liters respectively. Estimating the cost of import for petrol and/or octane at BDT 35.0 per liter¹ [55,56], using fuel blends containing 5 percent bioethanol will save about 970 million BDT annually (equivalent to about \$11.80 million USD per year) and using blends containing 10 percent bioethanol will save about 1.94 billion BDT annually (equivalent to about \$23.67 million USD per year). Table 10 enlists the annual consumption (2016-17) of petrol and octane and the possible savings of foreign exchange.

Table 10: Annual consumption (2016-17) of Petrol and Octane and possible savings for bioethanol blending.

	Unit	Petrol	Octane
Annual consumption in 2016-20117	Metric Tons	232,359	186,911
Using E5 will reduce annual petrol and octane consumption	Metric Tons	11,620	9,345
	Million Liters	15.37	12.36
Using E5 will save foreign currency per year	BDT	970 million	
	USD	11.80 million	
Using E10 will reduce annual petrol and octane consumption	Metric Tons	23,235	18,690
	Million Liters	30.73	24.72
Using E10 will save foreign currency per year	BDT	1.94 billion BDT	
	USD	23.67 million	

Considering the current crude oil price, the production cost of bioethanol (85 BDT per liter; ref: Sunypun Organics Limited) will be higher than the production cost of either petrol or octane. However, the price of petroleum fuel is not immutable since the global oil market is always fluctuating and causing the fuel price to be constantly in a flux [15]. Factors such as global political conditions and demand for oil might affect the fuel price. On the other hand, adoption of newer technologies will inevitably reduce the cost of bioethanol production. Since 2001, energy requirement in bioethanol production process has decreased by 28 percent, electricity requirement by 30 percent while bioethanol yield has increased by 5.3 percent [16]. Moreover, gasoline production is more energy-intensive than bioethanol. One unit of fossil energy used in the corn ethanol production process results in 2.3 units of energy in the form of ethanol while it takes 1.23 units of fossil energy to produce one unit of energy in the form of gasoline [57][16]. Moreover, the use of bioethanol blend petrol and octane result in improved engine performance than with only petrol or octane [7].

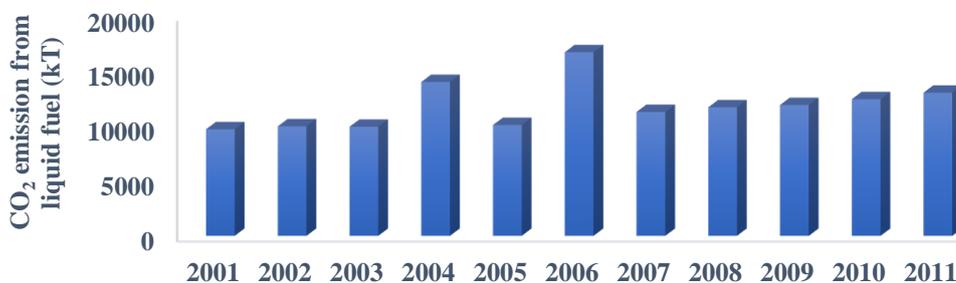


Figure 15: CO₂ emission from liquid fuel in Bangladesh [58].

The current CO₂ emission in Bangladesh from the combustion of liquid fuels is alarming from the environmental viewpoint (Figure 15). In 2016, Bangladesh Government signed the Paris Agreement, agreeing to mitigate CO₂ emission by way of using renewable sources using national and international support [59]. The use of bioethanol blends may reduce GHG, CO, NO_x and particulate emission [7]. Also, bioethanol production plant can provide employment to a wide range of workers in a variety of occupations (Renewable Fuels Association). Thus, bioethanol, produced from locally available biomass, can serve as a potential alternative fuel source and contribute to the sustainable development of Bangladesh.

5.3 Availability of Raw Materials: Impact on Food Cycle in Bangladesh

To replace 10 percent of the combined annual consumption of petrol and octane, about 80 million liters of bioethanol will be required annually. A plant capacity of 245,000 liters per day, operating 330 days per year, will meet the required demand. Locally available raw materials under consideration are corn, broken rice, and molasses. Figure 16 shows a comparison between the requirement and availability of the raw materials for bioethanol production in Bangladesh for a plant capacity of 245,000 liters per day.

¹ FOB Price of premium gasoline = 560 \$/t and Freight Cost (Middle east – east Asia) = 10 \$/t
\$1 = BDT 82 and Density of Petrol & Octane = ~ 0.756

Maize: Annual maize production in Bangladesh was 2.45 MMT in 2015-16 [60]. Generally, maize/corn contains around 16 percent moisture (Rana), which indicates that annual dry maize production is around 2.06 MMT. 1 ton of dry corn grain yields 124.4 gal or 470 liters of ethanol [61]. Therefore, for a plant producing 245,000 liters of bioethanol each day, 205,000 tons of corn is required per year. Even though Bangladesh grows more than enough maize for bioethanol production (only around 8 percent of the produced maize is required), in accordance with government regulation, bioethanol plants must use imported maize as raw material [54].

Broken rice: In 2015, annual paddy production was of Bangladesh 52,505,000 tons and milled rice production was 35,000,000 tons in 2015 [62]. Upon milling of Asian rice or paddy rice, around 8 percent to 16 percent of broken rice is produced [63][64][65]. Making a rather conservative assumption that 5 percent of the total rice produced yields broken rice during milling, annual broken rice production in Bangladesh is around 2.63 MMT (year 2015).

15 lb (6.8 kg) of starch yields about 1 gallon (3.79 liter) of fuel ethanol [66]. Since rice contains around 51% starch [67], to run a plant producing 245,000 liters bioethanol per day, 285,000 tons of broken rice is needed annually. In Bangladesh, broken rice is currently used primarily for making rice flour, and as poultry feed. Low-income people in Bangladesh also consume broken rice to some extent. However, even if broken rice was used as the sole raw material for producing bioethanol, less than 11 percent of the total broken rice produced in Bangladesh would be required, which is highly unlikely to affect the food security of the country.

Molasses: In Bangladesh, average annual molasses production is around 100,000 tons [68]. 1 ton of molasses yields 72 to 88 gallons of ethanol [69]. Using molasses as the only raw material for producing bioethanol in a plant with a daily production capacity of 245,000 liters is not possible since it will require at least 240,000 tons of molasses, which is much higher than the current molasses production of Bangladesh. Therefore, production of bioethanol using molasses exclusively as the raw material will warrant import of molasses from overseas. However, using all potential raw materials for bioethanol production that are available in Bangladesh in an alternating fashion and in a ratio based on their availability might prove to be a more cost-effective solution.

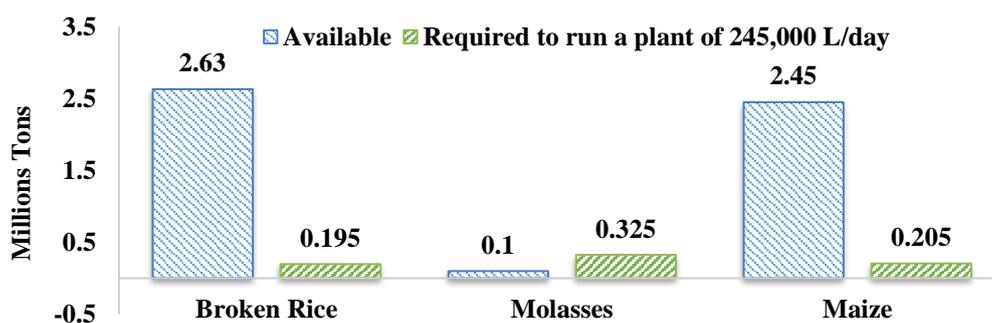


Figure 16: Raw material for bioethanol production: available vs. required.

6. Conclusion

Bioethanol blend petrol and octane are in the early stages of development in Bangladesh. On an energy basis, bioethanol has lower calorific value than petrol and octane; hence, relatively higher amount of bioethanol blends is required to get the same performance as octane or petrol. However, as seen from the experimental results, if fuel blends with low percentages of bioethanol (up to 20 percent) are used, calorific value is not significantly affected. Also, at low blend ratios, changes in fuel properties do not warrant any engine modification. However, corrosion protective measures (corrosion inhibitor etc.) are recommended when bioethanol blends at 10 percent or higher blend ratios are used. The current cost of production of bioethanol is greater than that of both petrol and octane. As a result, the cost of using bioethanol as a substitute for either petrol or octane is higher than the current cost of fuel. However, application of new and improved technologies can bring down the cost of production of bioethanol. Furthermore, bioethanol blends can significantly reduce greenhouse gas emissions over their entire life cycle. Thus, using bioethanol to replace petrol and octane is favorable from the environmental viewpoint. According to this study, using bioethanol blends at low blend ratios (up to 10 percent) is unlikely to affect the food security of the country since, compared to the country's production, the raw material requirement is very low. Also, as analyzed in the study, bioethanol blend fuels will reduce dependence on imported petroleum products and save foreign currency. In addition, bioethanol production facilities will create job opportunities for local people. Thus, locally produced bioethanol can have a significant impact on reducing the country's dependence on foreign resources while securing a better environment for future generation.

Acknowledgements

This research was supported by BCEF Academic Research Fund and CASR Research Fund. The authors would like to acknowledge Sunypun Organics Limited, Bangladesh for bioethanol samples, and Mr. J. Bishwash of Fuel Lab, ChE, BUET, for providing technical support.

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Energy Recovery from “Spent Wash” of Alcohol Distillery: A Case Study of Carew & Co. Ltd.

Md Hasan Shahriar Raby, Mostofa Shoroar Shuvo, Salma A. Iqbal, Md Shahadat Hossain*

Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology, Sylhet-3114, Bangladesh

Received: 16 August 2021; Accepted: 6 January 2022; Published: 30 April 2023

Abstract: Wastewater generated from distillery industry, known as the “spent wash,” is one of the most important factors for environmental degradation. The wastewater is highly concentrated, characterized by high chemical oxygen demand (COD) (up to 80–100 kg O₂/m³), low pH (up to 4.38), high biological oxygen demand (BOD), phosphorus, ammonia, metal ions like copper and iron, as well as complex organic materials such as lignin, yeast cells, protein, etc. One of the methods of management of distillery spent wash is anaerobic fermentation with the production of biogas, which is an alternative source of energy beyond fossil fuel. This study mainly focuses on analysis of the production rate of biogas by batch anaerobic fermentation process, quantification of biogas with respect to spent wash feed, and energy recovery from spent wash. The energy found in this study was equivalent to 7.535 W-h, per litre of spent wash. This study suggests that spent wash from distillery industry can be fermented to produce biogas, which will serve as an alternative source of energy and address energy crisis and environmental degradation issues.

Keywords: *distillery industry, spent wash, anaerobic fermentation, chemical oxygen demand, biological oxygen demand.*

1. Introduction

Energy demand is rapidly increasing worldwide. Statistically, in 2000 and 2019 world’s total energy consumption were 27,417TWh and 43,849TWh respectively which indicates 60% increase in consumption with respect to 2000 [1]. As for environmental pollution concerns, the European Union aims to reduce total greenhouse gas emissions in developed countries up to 80-95% by 2050 [2]. Likewise, for growing energy demand, exploration of alternative source for energy is mandatory. It is found that total biofuel consumption increased around 900% from 2000 to 2019 [1]. The factors that initiates the need for switching towards renewable and alternative energy sources are energy prices, population increase and climate change issues [3]. And for these reasons, renewable sources of energy are considered as one of the emerging sources of energy.

Use of biogas as renewable fuel source for vehicles is growing in Sweden as well as in Switzerland, and there is rising demand in other countries, including Austria, France Spain, Germany, USA, China and India [4]. By utilizing biogas for the electricity production, huge amount of greenhouse gas emissions are reduced [5]. Distillery effluent wastewater contains large quantities of soluble organic matter and plant nutrients [6]. So, the residual organic content can be used as fertilizer after anaerobic treatment. The pH level, nutrient level, etc. also meets the amendment of soil after treatment.

On the other hand, alcohol distilleries are extensively growing due to widespread industrial applications of alcohol in pharmaceuticals, food, perfumery, etc. It is also used as an alternate fuel. With the highly increasing demand of alcohol, highly polluted wastewater is being generated having musty odor and dark brown color. As for example, the Carew & Co produce more than 150,000L of effluent per day for producing ethanol and spirit. The pollution load of these waste streams and large amount of spent wash being discarded directly to the environment make the alcoholic beverage industry a highly polluting one. [7]. It can damage river water quality. The concentration of inorganic substances such as nitrogen, potassium, phosphates, calcium, sulphates is also very high [8]. The unpleasant odor of the effluent is due to the presence of skatole, indole and other sulphur compounds, which are not effectively decomposed by yeast during distillation [9].

The four main phases in manufacturing alcohol in distilleries are feed preparation, fermentation, distillation, and packaging [10]. Ethanol can be produced from a variety of biomass sources, but their utility as feedstock is determined by their cost, availability, carbohydrate content, and ease of conversion to alcohol [11]. Sugar crops account for over 61 percent of global ethanol production [12]. Proper sugar content can be obtained from molasses. It is then complemented with a nitrogen source that can be assimilated, such as ammonium sulphate or urea. If necessary, it is further augmented with phosphate. Sulphuric acid is used to lower the pH of the fermentation broth to below 5. Fermentation is carried out with an active culture of *Saccharomyces cerevisiae*. In the fermented mash, ethanol can accumulate up to 8%–10% by volume. After the yeast sludge is discarded, the fermented mash is distilled, fractionated, and rectified. Spent wash [13] is the leftover portion of the fermented mash that emerges as a liquid effluent.

Spent wash disposal into the environment is hazardous as it has a high pollution load. High COD, total nitrogen, and total phosphate level of the effluent may lead to eutrophication of natural water bodies [14]. It also has adequate levels of micronutrients such iron, zinc, copper, manganese, boron, and molybdenum [15]. Colored components of the spent wash impede sunlight penetration in rivers, lakes, and lagoons, lowering photosynthetic activity and dissolved oxygen concentrations and harming aquatic life [16]. Disposing distillery spent wash on land is also detrimental to the environment. It impedes seed germination by diminishing soil alkalinity and manganese availability [14].

There are one of another technique to reduce COD concentration, as well as complex organic materials such as lignin, yeast cells, protein by utilizing this waste as raw material of biogas production. There is different technique involved in biogas generation like anaerobic lagooning, high-rate anaerobic reactor such as fixed film reactor, UASB reactor, fluidized bed reactor, batch reactor and aerobic system etc. [17] One of the methods of distillery spent wash utilization

* Corresponding Author: Md Shahadat Hossain,
E-mail: shahadat_cep43@yahoo.com

is anaerobic fermentation with the production of biogas which is an alternative source of energy after fossil fuel as the storage of fossil fuel is curtailed. Biogas produced from anaerobic digestion of wastes contains a large amount of methane, typically 50-65%, having a high calorific value. It can be used for the production of electricity, heat and power [18]. Conventional treatment processes of spent wash have a number of advantages, but consequently, more effective microorganisms that can decolorize effluent and can be used as the primary source of nutrients without considerable dilution are needed. Both color and COD can be removed using physicochemical treatment procedures. However, these systems have drawbacks such as excessive chemical consumption, sludge production with subsequent disposal issues, and high operational expenses [15].

1.1. Anaerobic Treatment Processes

A typical COD/BOD ratio of 1.8–1.9 indicates the suitability of the effluent for biological treatment [19]. Anaerobic treatment of distillery effluent is an accepted practice and various high-rate reactor designs have been tried at pilot and full-scale operations [20].

Anaerobic digestion is considered as a complex ecosystem in which methane and carbon dioxide are generated by physiological activities of a distinct groups of microorganisms. It has a strong degradation capacity for concentrated and refractory compounds. It generates very less sludge, uses less energy, and can be economic if considerable amount of biogas can be cogenerated [21]. These mechanisms, however, have been found to be susceptible to organic shock loadings, low pH, and anaerobic microbe growth rates, resulting in extended hydraulic retention durations (HRT).

Single-phase and bi-phase anaerobic systems are both viable. A biphasic system can optimize fermentation procedures of each stage in its own fermenter. As a result, the total process efficiency and kinetics are better than those of single-stage processes.

The treatment of distillery effluent in CSTR has also been reported in single and biphasic operations, with COD reductions up to 80–90% in 10–15 days [22]. To achieve an acceptable amount of deterioration, very high HRT values are required. Because of high HRT values, the CSTR approach for wastewater treatment is less feasible.[23]

In fixed film reactors, the biomass attachment is reinforced by a biofilm support structure (media).

The advantages of a fixed film reactor are ease of construction, absence of mechanical mixing, improved stability at increased loading rates, and the capacity to absorb toxic shock loads. After a period of deprivation, the reactors can swiftly recover [24].

In recent years, numerous categories of wastewater have been effectively treated using the Upflow Anaerobic Sludge Blanket (UASB) technique [25]. UASB reactor systems fall under the category of high-rate anaerobic wastewater treatment, making them one of the most widely used reactor designs for distillery wastewater treatment worldwide. The development of active and settleable granules is critical to the effectiveness of UASB [26]. The granules are made up of self-immobilized anaerobic bacteria into compact forms. This improves biomass settleability and results in effective bacteria retention in the reactor [27]. The UASB reactor design has several appealing qualities, including its independence from mechanical mixing of digester contents, the recycling of sludge biomass [28] and ability to cope up with perturbances caused by high loading rates and temperature fluctuations [29]. The UASB technology is well suited for high strength distillery wastewater only when the process has been successfully started and is in stable operation.

In the anaerobic fluidized bed reactor (AFB), the drag forces imposed by the up flowing wastewater keep the medium for bacterial adhesion and growth fluid. Sand with tiny particles, activated carbon, and other media are employed. Each medium provides a significant surface area for biofilm formation and growth whenever it is fluidized. It allows for a high reactor biomass holdup, also improving system efficiency and stability. Fluidized bed technology is an excellent anaerobic method for treating high-strength waste fluids because it promotes the transfer of microbial cells from the bulk to the surface, increasing the interaction between microorganisms and the substrate [30].

Batch reactor treatment for distillery wastewater has not been widely used. The reactor's potential, operating feasibility, and scale-up need to be investigated. In this study, an anaerobic sequencing batch reactor (ASBR) was used to explore the treatment of winery wastewater [31].

Despite numerous additional research on other approaches, as discussed above, the study with batch anaerobic process is insufficient to make any further decisions about its use in commercial or large-scale applications. Hence, this technology was selected for research in order to explore probable options in the renewable energy sector.

2. Materials and Methods

2.1 pH adjustment and Reactor setup

As the pH of spent wash was 4.38 which was too low to grow microorganisms involved in anaerobic fermentation, 2M NaOH was used to adjust the pH in 6.7.

For batch reaction process, 4L pH adjusted spent wash and 100gm cow dung as inoculum were added in a 5L bottle. After that, an agitator at 400-500 rpm speed was set-up and the bottle was made airtight to inhibit air insertion.

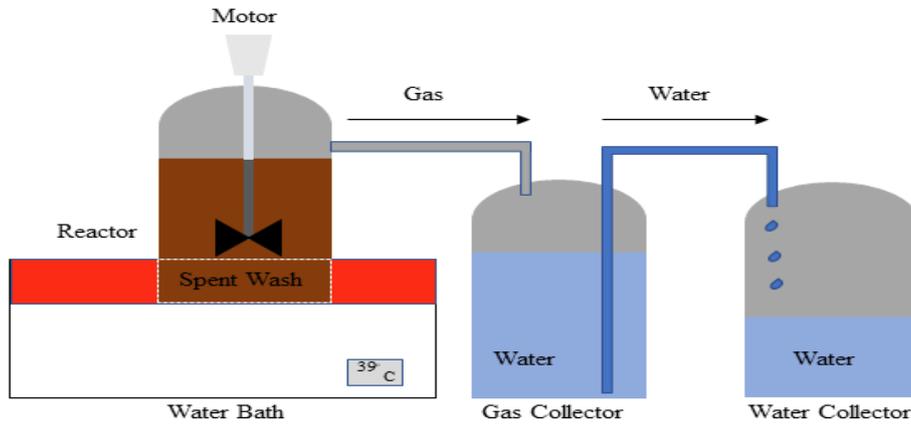


Figure 1: Experimental setup.

2.2 Gas and water collector setup

There were two hose pipes, one for gas collection from reactor to gas collector and another one for displaced water collection from gas collector to water collector. The pipe between two collectors was adjusted in such a way that both sides of this pipe was dipped in water, hence air could not enter into the reactor by back flow. Then the reactor was taken into a water bath to maintain a temperature of 39 degree centigrade as shown in figure 1.

2.3 Energy estimation for produced biogas

After producing biogas, the focus of this study was to estimate the total energy and power generation from the treated waste.

Total biogas produced and total power recovery can be calculated by following equations.

- Total methane content (mole) = Total biogas production (mole) × methane percentage / 100
- Power generation from produced methane (KW h/L spent wash) = heat content (KW h /mole CH₄) × total produced methane (mole) / spent wash volume (L)

3. Results and Discussion

The produced gas was collected every day from gas collector after day 1 from run. Overall production of gas per liter of spent wash was 1.28L. Figure 2, shows that during the first two days, the production was not enough but after three days it showed a peak production which was 58.1% more at day 3 than day 2 and increasing trend was continued till day 4.

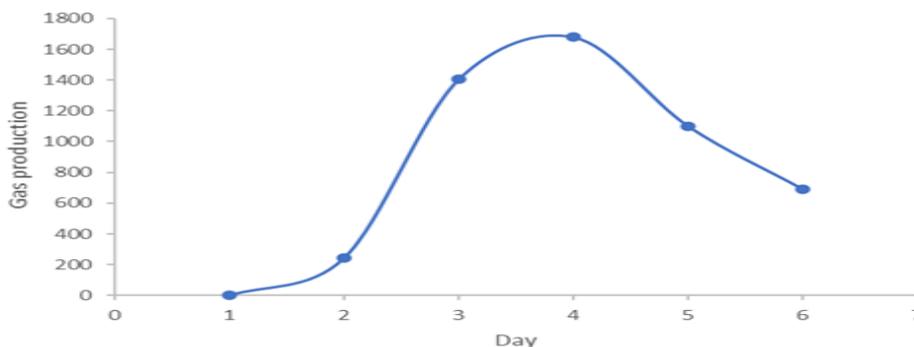


Figure 2: Gas production from batch process of anaerobic Fermentation.

Number and growth rate of microorganism growth are crucial factors to increase gas production. During the first two days there was not enough microorganism to produce maximum amount of gas but with passage of time the growth and number of microorganisms were increased to its optimum position to produce maximum amount of gas on day 4. But after peak result, it showed a downfall of gas production, 53% decrease at day 5 compared to day 4 as the death rate of the microorganisms was more than growth rate.

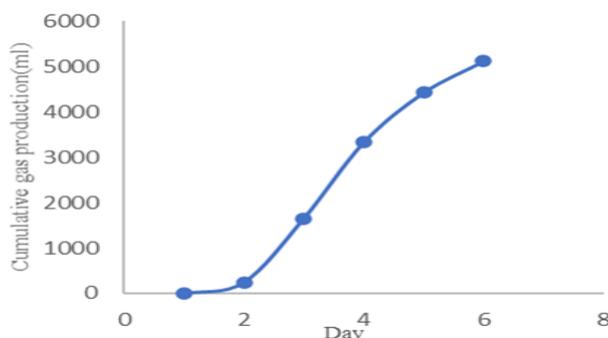


Figure 3: Cumulative gas production

Figure 3 represents the total gas produced in cumulative way, which was 5.1L after 6 days of production. The gas composition analysis was conducted by Gas Chromatograph (GC) (Model 2014, Shimadzu, Japan). In GC analysis, following conditions were used for the methane, nitrogen, and carbon dioxide content measurement: column temperature – 60°C, pressure – 375 kPa, and gas flow rate – 55 ml/min. The result found from this analysis is shown Table 1. This experiment was conducted in anaerobic batch process and [32] process was ran by up flow anaerobic sludge blanket (UASB) method. For this reason the composition may vary in CH₄ and CO₂ contents from the reference values.

Table 1: Comparison analysis of biogas composition

Gas Components	Study values (%)	Reference values [32] (%)
CH ₄	53	57
CO ₂	30	23
N ₂	15	15.6
Others	2	4.4

3.1. Methane production and energy estimation

For conversion of biogas units from L to K mole, ideal gas law was used which states that pressure times volume is equal to mole times gas constant times temperature in Kelvin unit.

- Total biogas production (mole NTP)

$$= 5.1\text{L} * (1 \text{ atm}) / (0.0821 \text{ L atm K}^{-1} \text{ mole}^{-1} * 298\text{K})$$

$$= 0.2085 \text{ mole NTP.}$$

- Total methane content (mole)

$$= 0.2085 \text{ mole biogas} * 53 \% \text{ CH}_4 / 100$$

$$= 0.11 \text{ mole CH}_4$$

To calculate heat production capacity of produced bio-methane from biogas, it was required to know the heat of combustion of per mole methane which is 889.2 kJ/mole and thus 0.247 KW h/ mole [33].

- Power generation from produced methane (W h/ L spent wash)

$$= 0.11 \text{ mole CH}_4 * 0.247 \text{ KW h/ mole} / 4\text{L spent wash}$$

$$= 7.535 \text{ W h/ L spent wash.}$$

From Table 2 it can be seen that the COD as well as nitrogen [35] is much higher, which means higher C/N ratio, as substrate to produce sufficient amount of microorganism as well as biogas found from experiment. The data obtained here might be analogous to sugarcane distillery plant.

As Carew and Co. Ltd. produce 160,000L/day spent wash, it is a huge opportunity to produce large volume of biogas which can meet one of the largest portions of gas necessity in Bangladesh.

Table 2: Characteristics of untreated and anaerobically treated distillery effluent [34]

Parameters (mg L ⁻¹)	Values for distillery effluent
pH	3.0–4.5
BOD ₅	50,000–60,000
COD	110,000–190,000
Total solid (TS)	110,000–190,000
Total volatile solid (TVS)	80,000–120,000
Total suspended solid (TSS)	13,000–15,000
Total dissolved solids (TDS)	90,000–150,000
Sulphate	7500–9000
Phosphate	2500–2700

4. Conclusion

As the energy problem is rising day by day globally and in Bangladesh, the need for alternate renewable energy source is growing day by day to fulfil the current demands. Furthermore, environmental problems are also increasing day by day and it is on its way to become one of the major threats to our flora and fauna, and hence it is urgent to reduce wastes to save the world. Reusing the waste and converting it into value-added products is a great way to reduce wastes. This study focuses on treatment of spent wash from Carew and Co. Ltd. and it was found that 53% CH₄ and 30% CO₂ was obtained after anaerobic treatment of spent wash and power equivalent to 7.535 W h was obtained from per Litre spent wash. From this experiment, it can be understood that biogas generation from distillery spent wash is a source for energy recovery as well as environmental conservation. This can save water bodies from pollution and can contribute to national energy grid to cover up a portion of our energy scarcity.

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A Material Balance Approach for Assessing Textile Chemical Consumption: A Case Study of Bangladesh Textile Sector

Md Mursalin Rahman Khandaker¹, Rathin Chakraborty², Mohidus Samad Khan^{1*}

¹*Environmental Sustainability in Textile Industries (ESTex), Department of Chemical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh.*

²*Institute of Appropriate Technology, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh.*

Received: 19 October 2022; Accepted: 14 January 2023; Published: 30 April 2023

Abstract: The textile and apparel industry around the world has developed greatly since the invention of cotton gin in the 18th century. It is an immense global market, worth USD 993.6 billion. Bangladesh is the second largest apparel exporter in the world. The textile industry of Bangladesh is the backward linkage industry of the country's \$38.7 billion apparel sector. This industry manufactures and exports a wide range of ready-made garments (RMG). All these garments require a series of wet processing stages, in which different chemicals are consumed in large amounts. But there is no tool for assessing textile chemical consumption pattern in Bangladesh. This article introduces a mathematical tool to assess textile chemical consumption at national level by using a material balance approach from fiscal year (FY) 2007-08 to 2019-20. It had been estimated that Bangladesh produced textile products weighing about 2.38 million metric tons consuming almost 1.75 million metric tons of chemicals, worth around 2 billion USD. The market share was found to be around 3.85 % with respect to global textile market share. This novel study quantifies the chemicals consumed by the textile sector of Bangladesh in a fiscal year. It considers the type and nature of the chemicals used in different wet processing stages and the economic aspects of the consumed chemicals. Further analyses might provide ideas for sustainable management of textile chemicals. This study will also help policy makers, investors, and entrepreneurs to drive production of textile chemicals in Bangladesh, thus reducing the import costs and facilitating sustainable business. **Keywords:** *textile chemical, annual production and consumption, material balance, sustainable chemical management*

1. Introduction

The textiles and garments industry forms an important element of global trade, particularly for developing and least developed countries. Bangladesh is one of the largest ready-made garment manufacturing countries of the world which has been driving the country's economy since 1990 and providing jobs for more than 50% of the total industrial workforce of the country (Khan, Brymer, & Koch, 2020; Project, 2020). The sector has experienced steady growth with the bulk order of value-added products of top-multinational apparel companies or brands during the last 30 years. This country is home to world's highest number of green factories and has been serving as a compliant sourcing hub for more than 150 countries (BGMEA, 2022). Bangladesh, being the world's second-largest Ready-Made Garment exporter after China, jumped by 15% to \$38.76 billion in the fiscal year (FY) 2020-21, after the sector took a roughly \$6 billion hit and came down to \$27.94 billion in the FY 2019-20 due to the outbreak of COVID-19 pandemic [20, 21]. Bangladesh apparel sector reached up to 81 percent value addition threshold relying on the strong backwardly linked dyeing and finishing facilities, reaching a new height of exports despite the hurdles faced [1, 5, 30]. Major exporting partners of Bangladesh ready-made-garments are :Germany United Kingdom, Spain, France, Italy, Poland, Netherland, Denmark, Belgium and Sweden for the FY 2019-20 [7].

Bangladesh textile dyeing industries are arguably the largest chemical consumers within the country, both in terms of commodity and functionality. Commodity chemicals are consumed in gross volumes (such as salts, alkali) and the functionality chemicals are used to accomplish specific purposes according to necessity [11, 23]. Hence, this industry involves thousands of chemicals of wide varieties with a specific purpose in processing and finishing operations [16, 19]. A typical dyeing process consists of the following sequence of operations: sizing, de-sizing, scouring, bleaching, mercerization, enzyme treatment, dyeing, wash-off and finishing [3, 28]. Textile chemical consumption depends on several factors, such as fiber, yarn or fabric composition, color, or depth of the shade, dyeing machinery, dyeing procedure, liquor ratio, finishing type and finally consumer requirements [24].

Almost 90% of the required textile chemicals are imported and around 10% of the chemicals are sourced locally. There is no dedicated national database and audit tool for identifying the source, import volume and corresponding usage of these textile chemicals. Besides, the economic aspect of these chemicals is also not well understood or documented. In order to ensure and promote sustainable consumption of chemicals throughout the value chain, a comprehensive understanding of textile wet processing stages (dyeing, printing, finishing and washing) and associated chemical usage is needed for the qualitative and quantitative analysis of textile chemical consumption.

In this article, material balance approach has been used as an audit tool to assess annual chemical consumption in Bangladesh textile dyeing industries. Material balance technique for chemical consumption calculation is a fundamental technique for estimating annual textile production, in terms of textile article export value, weight per piece of garment and average price of per piece of garment. For this approach, representative factories have been selected with definite production processes (knit, woven, denim and yarn dyeing) and annual consumption of chemicals for those wet processing facilities have been calculated. Then those values were scaled up for obtaining the total volume of chemicals consumed in a fiscal year.

* Corresponding Author: Mohidus Samad Khan,
E-mail: mohid@che.buet.ac.bd

This article generates a chemical consumption audit tool and a database for Bangladesh textile industries analyzing the consolidated prospects of its usage, growth and forecast in the world market. It also analyzes the economic aspects of textile chemicals consumed in Bangladesh. A database indicating the types, quantity, origin, transportation, storage, handling and usage of the textile chemicals can provide a clear understanding of the chemicals consumed in Bangladesh in a fiscal year. This audit tool may act as a backbone of implementing sustainable management of textile chemicals. This study presents a holistic approach towards preparing a database for textile chemicals that are consumed in Bangladesh. It might help textile industries to better monitor and maintain chemical inventory, explore and implement chemical safety and security options, phase out restricted chemicals and use eco-friendly options.

2. Textile Wet Processing in Bangladesh

Textile wet processing is a branch of applied chemistry in which different chemicals, dyestuffs and pigments are applied to textile materials for achieving a desired hue and design. It involves mechanical and chemical treatment to improve the aesthetic value of the fiber, yarn, fabric and garment [17, 29]. Textile finished product is a result of the long manufacturing chain, and the stages involved are – fiber, yarn, fabric, wet processing, and garments manufacturing. Textile wet processing practices in Bangladesh include knit dyeing, woven dyeing, yarn dyeing, denim dyeing, printing and garments washing. The application of coloration varies with different fabric construction, but the basic principle is similar for all kinds of textile articles. Figure 1 represents the general process sequence of fiber to end products in the textile industry and Figure 2 describes the textile chemical supply chain, from port to factory gate.

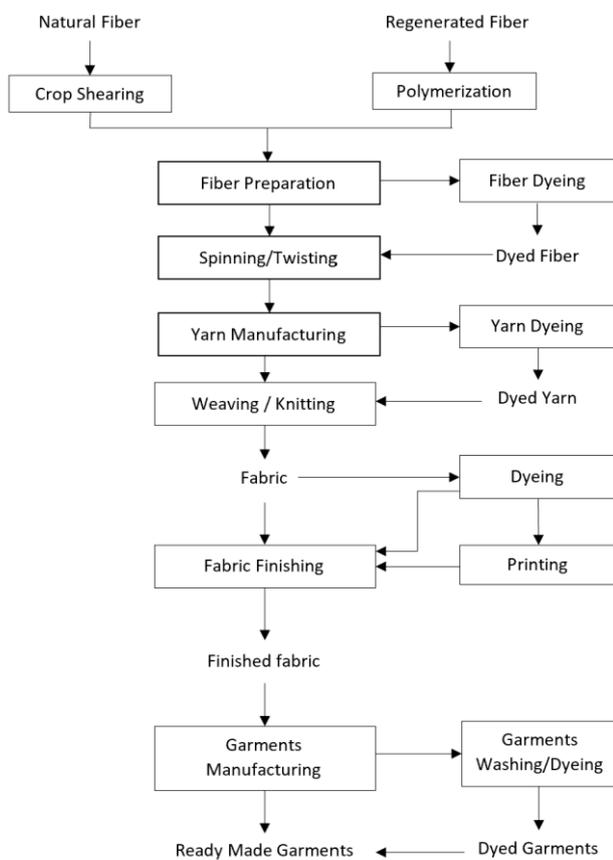


Figure 1: A typical textile manufacturing chain

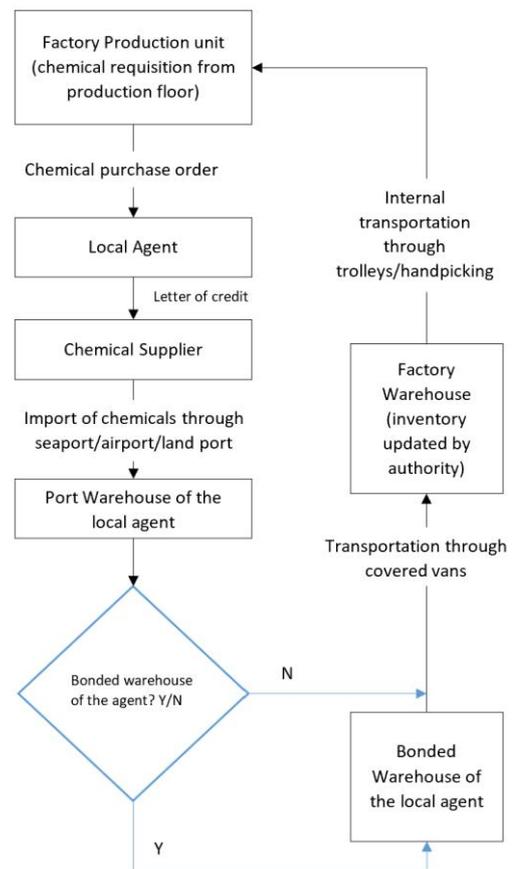


Figure 2: Textile chemical supply chain [10]

2.1 Knit dyeing

Knitting is the method of fabric formation by inter-looping of one or one set of yarns (Spencer, 2001). The batch or exhaust dyeing process is commonly practiced in Bangladesh for coloring of knitted textiles. The performance of dyeing depends on the quality of chemicals. Figures 3, 4 and 5 illustrate the type of chemicals consumed in different types of knit fabric processing units of Bangladesh. Basically, coloration of cotton fabric is done by reactive dyestuff, optical brightening agent is used for whitening of cotton fabric and disperse dyestuff is used for coloration of 100 % polyester fabric. Before finishing, final quality check (QC) is done to ensure that no extra chemicals are needed. If the fabric fails to meet the final QC, the shades are revised, and chemicals are adjusted according to need.

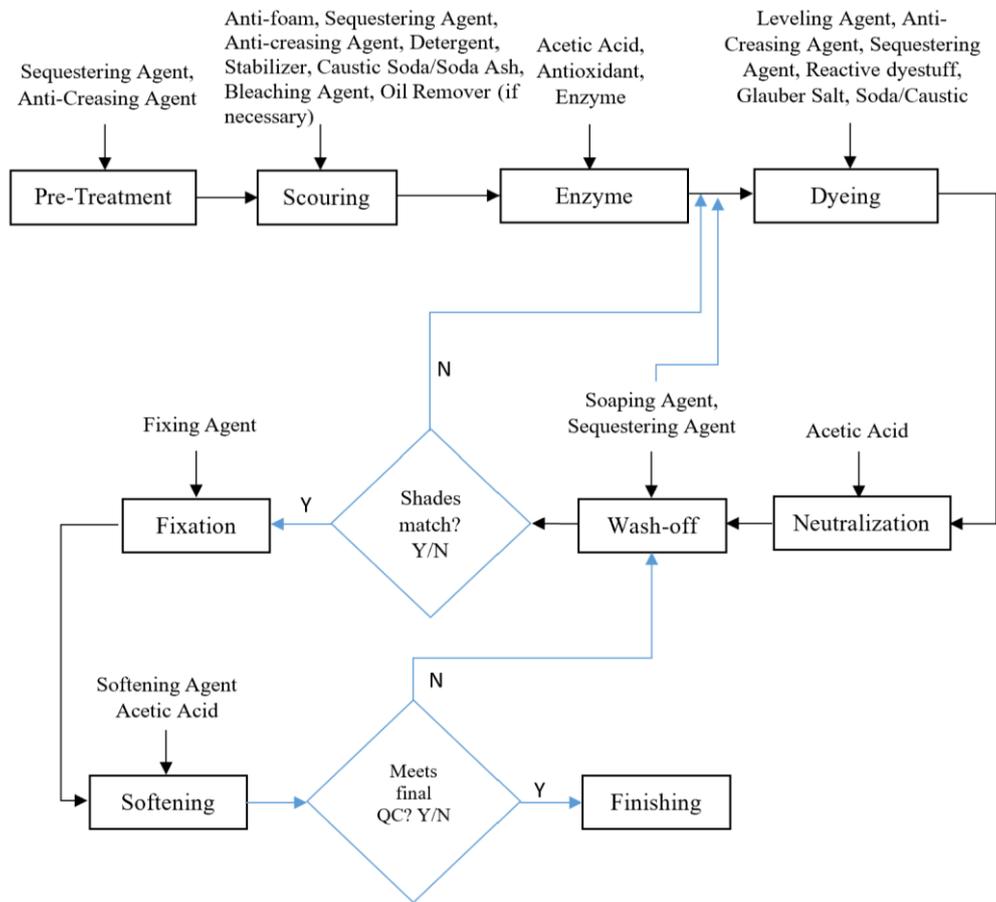


Figure 3: Process sequence and chemical use of cotton knit dyeing (Colored fabric)

Generally, cotton and polyester fabric are mostly dyed in Bangladesh dyeing industry. Reactive dye is a widely used dyestuff for cotton and disperse dye is the universal dyestuff for polyester in knit dyeing industry. Dyeing procedure of polyester fabric is much more complicated than dyeing of cotton fabric. In case of polyester dyeing, high temperature and pressure have to be maintained for good quality products [14].

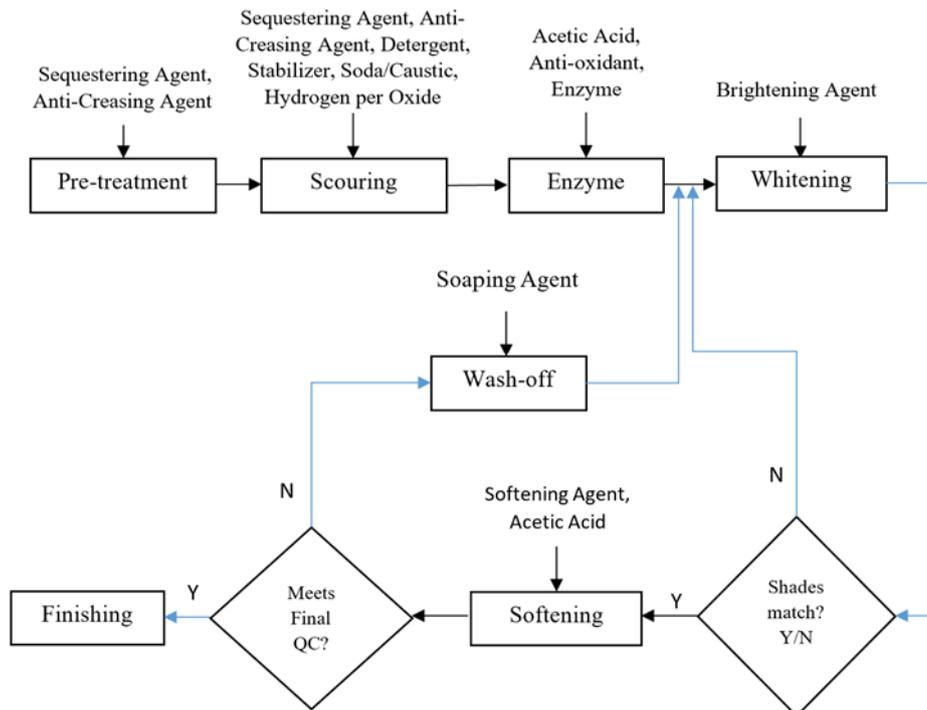


Figure 4: Process sequence and chemical use of cotton knit dyeing (White fabric)

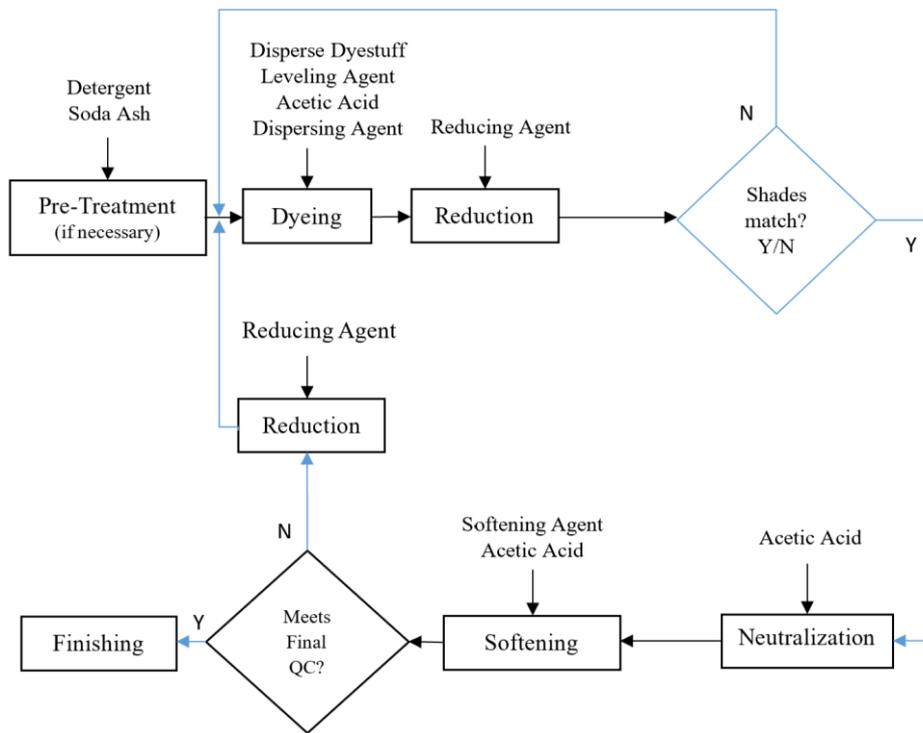


Figure 5: Process sequence and chemical use of 100% polyester knit dyeing

2.2 Woven dyeing

Weaving is a method of fabric formation by intersection or interlacement of two sets of yarns (warp and weft), which cross at right angles to each other[2]. The main technique or process used in woven dyeing fabric is the continuous dyeing process. Color retention of woven fabric may be processed by pad dyeing [22], jigger dyeing or jet dyeing[18,22]. Generally, mercerization of woven fabric depends on the buyer requirements. Liquor-ratio, temperature and dwell time are the fundamental factors of uniform woven dyeing. At present, a diverse range of design and structure-oriented woven fabrics are produced in Bangladesh. Figure 6 illustrates the chemicals involved in each stage of woven textile processing units (coloration of cotton fabric with reactive dyestuff of Bangladesh).

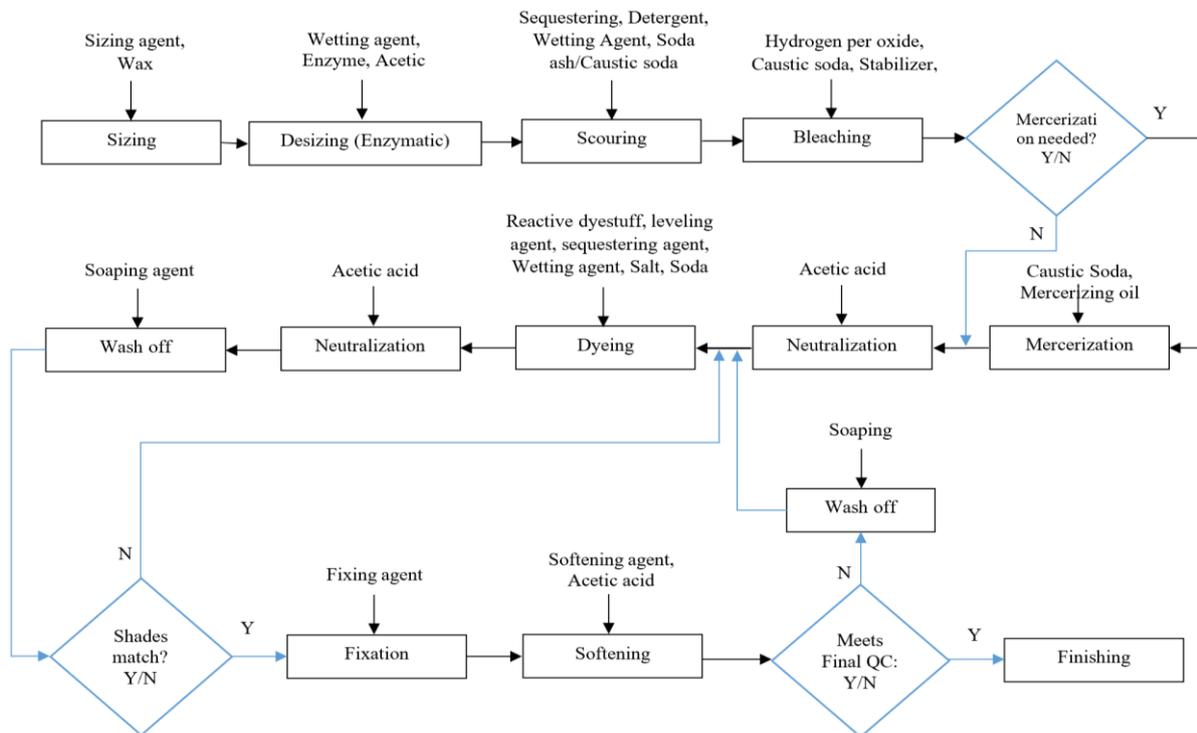


Figure 6. Process sequence and chemical use of cotton woven dyeing (color)

2.3 Denim dyeing

Denim is a stable, durable fabric constructed in a twill weave in which the warp threads are dyed while the weft thread is left undyed[4, 27]. There are different alternative dyeing methods that are used to obtain specific fabric appearance or performance. In Bangladesh denim industry, most of the denim fabrics are produced with 100% cotton and cotton-based blends with polyester or tencel, lycra and nylon etc. Figures 7 and 8 illustrate the nature of chemicals used in each stage in denim processing units (coloration for cotton yarn with indigo and sulfur dyestuff of Bangladesh. There are basically three types of denim warp dyeing in the continuous form: rope form, slasher and loop[25]. In Bangladesh, slasher and rope dyeing forms are used to manufacture denim products. The rope dyeing method is more suitable than slasher dyeing for a higher production rate with better quality dyeing, better wash fastness property, less breakage of ends and better shade consistency. But in contrast, more handling of yarn is needed to open ropes before sizing [8]. Denim washing is one of the most widely used finishing treatments in denim industry. Currently denim washing is done into two ways – mechanical washes (stone wash and sand wash) and chemical washes (acid wash, bleach wash, caustic wash, enzyme wash and pigment wash [4].

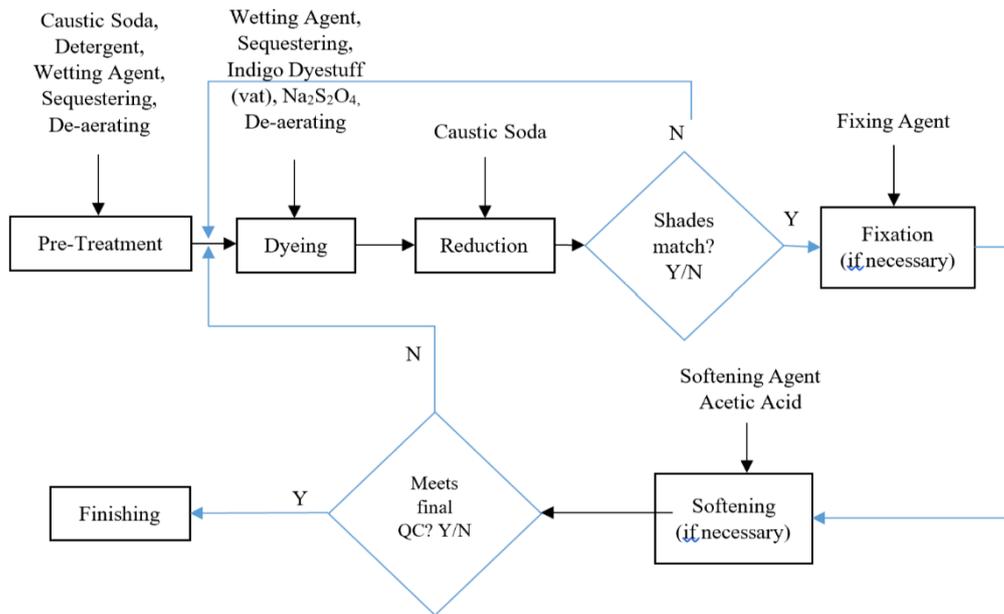


Figure 7. Process sequence and chemical use of denim indigo dyeing (Rope form)

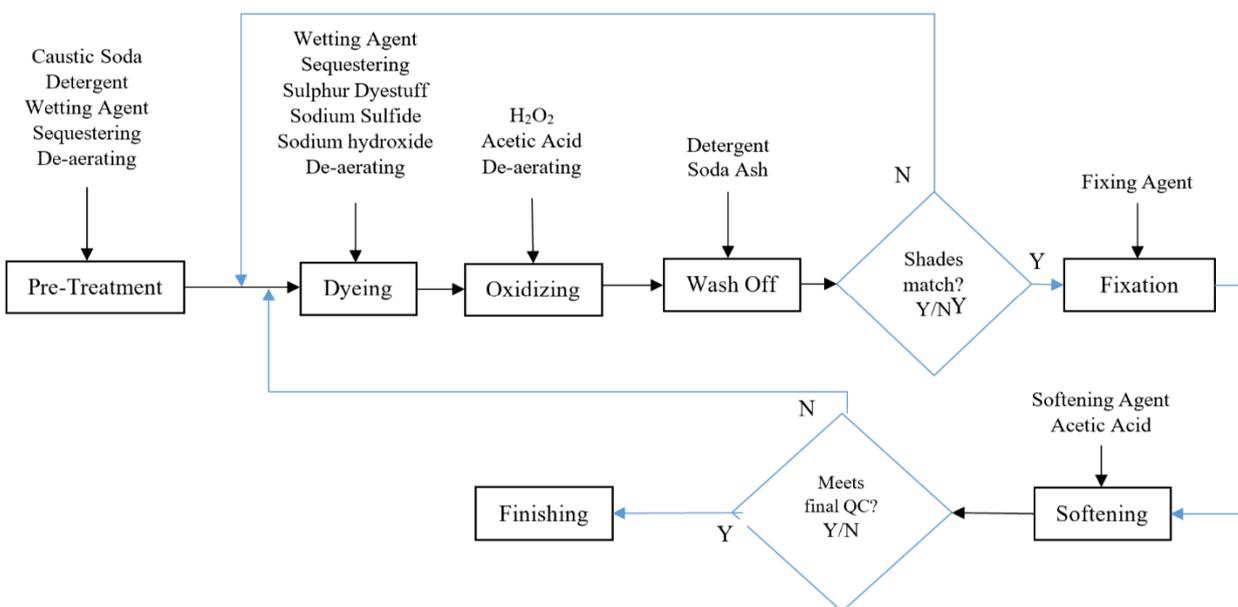


Figure 8. Process sequence and chemical use of denim sulphur dyeing (Rope form)

2.4 Yarn dyeing

Yarn dyeing is a method of coloration in which the yarns are dyed before they have been knitted or woven into fabrics. The main concern in dye selection for yarn dyeing is always the profitable production of a level dyeing with appropriate fastness properties[12]. At present, there are several forms of yarn dyeing methods in practice in the Bangladesh textile industry, namely – skin or hank dyeing, package dyeing, warp-beam dyeing, and space dyeing. The main purpose of yarn dyeing is to penetrate the dyestuff into the fibers, in the core of the yarn. The process sequence of applying color on yarn is alike the knit dyeing process.

2.5 Printing

Textile printing is a localized application of different dyes or pigments and chemicals by different methods (block, roller, screen, ink-jet, direct, resist, discharge, transfer, pigment, burn-out) to different specific areas on the face of a fabric according to predetermined color design[7, 15]. This is commonly attained by applying thickened pastes containing dyes or pigments onto a fabric surface according to the required design[7]. It is a technique of adding color to textile fabric to make decorative patterns. Figure 9 shows the chemicals involved in each stage in printing processing units of Bangladesh. After conducting surveys in several textile manufacturing units, it was estimated that around 40% of woven fabric and 30% of knit fabric were annually printed in Bangladesh textile industry.

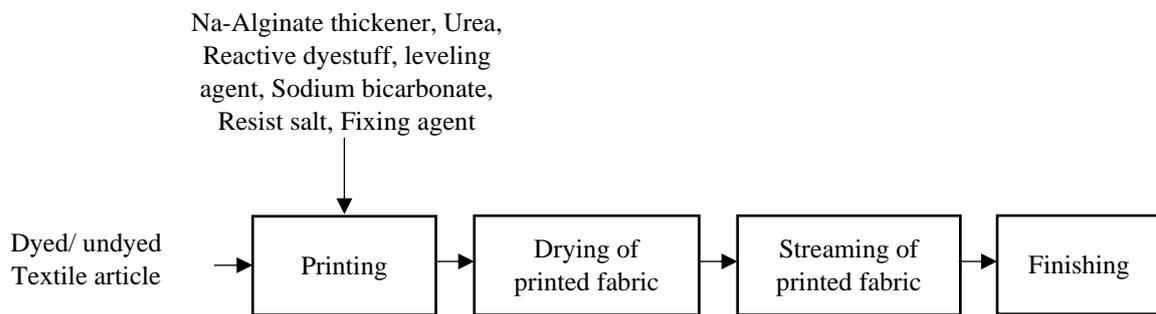


Figure 9. Process sequence and chemical use of printing (Cotton)

2.6 Garment dyeing

Garment dyeing industry, known as the “garments washing industry” is the process of dyeing assembled garment[9]. It is a method of coloration of fully fashioned garments (after stitching) The technique involved in garments dyeing is similar to the standard batch dyeing procedure, where garments are already prepared from either greige or scoured fabrics. The types of garment products such as sweaters, hosiery, T-shirts, socks and trouser are mostly in non-tailored forms. There are various methods used for garment-dyeing, such as cold dyeing, dip dyeing, over-dyeing, reverse dyeing, tie-dyeing, top dyeing, and normal wash.

3. Textile Chemical Consumption by Material Balance Approach

In this study, shirts, trousers, jackets and relevant items were considered as woven fabric, t-shirts and relevant items were considered as knit fabric, and sweaters and relevant items were considered as yarn dyed fabric by consulting with factory personnel. Export value of woven and knit fabric was sourced from online resources shared by the Bangladesh Garment Manufacturers’ and Exporters’ Association (BGMEA). Average export price and weight for per piece woven and knit fabric were assumed by contacting relevant factory personnel and buying-house merchandizers and from web resources. Apparel items exported from Bangladesh, prices of those items and market share have been enlisted in Appendix A1. An average of item wise product weight (textile products for men, women, and children), average weight of each of those products and their export price in USD has been shown in Appendix A2.

Total fabric production calculation (in million metric ton) was based on the following formula,

Total fabric production

$$= \frac{\sum(\text{Product Export value} \times \frac{\text{Weight}}{\text{piece}})}{\text{Avg.Price per piece} \times 1000 \times 1000} \times \text{Manufacturing Wastage } 20\% \quad (1)$$

For identification of chemical consumption per kg of knit, yarn, woven and denim products, firstly representative factories were selected for each type of product and then their dyeing processes were evaluated. Appendix A4 depicts the data for process wise monthly production and chemical consumption report of textile dyeing industries for the fiscal year 2019-20. The annual production and chemical consumption data were evaluated based on monthly production and chemical consumption report obtained from textile industries through visits, interviews and inspections. The data has been shown in Appendix A4. Amount of chemical required on an average to produce per kg fabric was based on the following formula:

Chemical Consumption

$$= \frac{\text{Amount of Annual Chemical consumption per year in kg}}{\text{Amount of Annual Production in kg}} \times 1000 \quad (2)$$

If amount of chemicals required to produce per kg fabric is known, total volume of chemicals consumed in the textile sector can be evaluated by multiplying with total production capacity of all the RMG factories in Bangladesh. Table A5 in Appendix A5 enlists the average amount of chemicals needed to produce per kg of fabric. Total chemical consumption in million metric ton of textile industry in FY: 2019 – 2020 had been calculated by multiplying total fabric production with chemical required to produce per kg of fabric. Finally, total amount of textile basic and auxiliary chemical consumption (in kilo ton) that were consumed in Bangladesh textile sector in the year of FY 2019-2020 was calculated by the following formula:

$$\text{Chemical consumption of textile industry (in kilo ton)} = \frac{\Sigma (\text{Annual Production} \times \text{Chemical Consumed per kg fabric} \times \text{Consumption percentage based on Annual Production})}{1000 \times 1000 \times 1000} \quad (3)$$

The total annual chemical requirement (in kilo ton) is the summation of chemical consumption data of knit, woven and denim dyeing industries of Bangladesh. By conducting factory visits, textile chemical market surveys, and by interviewing senior merchandizers and chemical responsible executives from ten (10) textile dyeing industries of Bangladesh, the average retail values of per kg chemicals (in USD) were identified. Multiplying the total annual chemical requirement with the average retail values of chemicals estimates the annual chemical market value in USD. Appendix A6 represents the breakdown of annual textile chemical consumption and market value analysis.

$$\text{Total Annual Chemical Requirement (in kilo ton)} = \Sigma (\text{Chemical Consumption}(\text{knit, woven and denim dyeing industries})) \quad (4)$$

$$\text{Annual chemical market value in million USD} = \text{Total Annual Chemical Requirement (in kilo ton)} \times \text{Average Price of Chemicals per kg in USD} \quad (5)$$

3.1 Textile Fabric Production

Generally, the apparel items for export can be categorized into two major categories- woven and knit apparel. These two categories broadly classify various types of garments, such as shirts, trousers, jackets, t-shirts, and sweaters, which constitute the major production share. Other items are also produced like lingerie, socks, swimwear, sports item, functional fabric etc. In FY: 2019-20, export earnings from Bangladesh ready-made garments were \$ 14.04 billion from woven garments and \$ 13.90 billion for knit garments according to a report from Export Promotion Bureau (EPB), which contributes about 83 % of the total export.

Table 1 and 2 represent the parameters and the calculation of knit and woven fabric production in Bangladesh.

Table 1. Knit Fabric Production Calculation (FY: 2019-2020)[5]

Parameter	Knit dyeing		Yarn dyeing
	T-Shirt/Single Jersey	OTHERS	Sweater/Pullovers /Cardigans
Product Export Value in Million USD, <i>PEV</i>	5614.00	4696.32	3597.68
Weight/Piece in gm, <i>W</i>	180	160	300
Average Price/piece in USD, <i>AP</i>	2.50	1.75	3.75

$$\begin{aligned} \text{Annual knit dyed fabric production} &= \frac{\Sigma(\text{PEV} \times \text{W})}{\text{AP} \times 1000 \times 1000} \times (\text{Wastage } 20\%) \\ &= \left(\frac{5614.00 \times 180}{2.50} + \frac{4696.32 \times 160}{1.75} \right) \times \frac{1.20}{1000 \times 1000} \\ &= 1.000 \text{ million metric ton} \end{aligned}$$

In fiscal year 2019-2020, it had been estimated by stakeholder consultation that yarn dyed apparels contributed to about 12.87 % of the overall readymade garment exports in Bangladesh. For calculation, it was assumed that all yarn dyed garments were produced from yarn dyeing industries in Bangladesh.

Hence, annual yarn dyeing production accounted up to 0.409 million metric tons in FY 2019-2020. $\left(\frac{3597.68 \times 300}{3.75} \times \frac{1.20}{1000 \times 1000} \right)$. Total knit dyed (exported) fabric production in FY 2019-2020 was 1.346 million metric tons (1.00 million metric ton + 0.345 million metric ton)

Table 2. Woven Fabric Production Calculation (FY 2019-2020)[5]

Parameter	Woven dyeing			Denim dyeing	
	Shirt	Trouser	Jacket	Other's	Denim
Product export value in million USD, <i>PEV</i>	1783.1	5447.13	3514.21	1135.41	2161.30
Weight/Piece (gm), <i>W</i>	250	300	400	200	300
Average Price/piece (USD), <i>AP</i>	3.25	3.50	3.75	1.75	3.50

$$\text{Annual woven fabric production} = \frac{\Sigma(\text{PEV} \times \text{W})}{\text{AP} \times 1000 \times 1000} \times (\text{Wastage } 20\%)$$

$$= \left(\frac{1783.14 \times 250}{3.25} + \frac{5447.13 \times 300}{3.50} + \frac{3514.21 \times 400}{3.75} + \frac{1135.41 \times 200}{2.00} \right) \times \frac{1.20}{1000 \times 1000}$$

$$= 1.628 \text{ million metric ton}$$

After conducting a survey with 10 top textile manufacturers and accumulating extensive information, it was found that around 40% of woven apparels and 75% of denim apparels were imported. If 40% woven apparels were imported, then annual woven dyed fabric production was 0.977 million metric tons and annual denim dyed fabric production accounted up to 0.228 million metric tons.

$$\left(\frac{2161.30 \times 250}{3.25} \times \frac{1.20}{1000 \times 1000} \right)$$

If 75% denim apparels were imported, then annual denim dyed fabric production was 0.057 million metric tons. Hence, woven apparel exported in FY 2019-2020 was 1.856 million metric tons (1.628 million metric tons + 0.228 million metric ton). Therefore, total woven dyed fabric production in FY 2019 – 2020 was 1.034 million metric tons (0.977 million metric tons + 0.057 million metric tons). From these calculations, it can be derived that the volume of apparel exported in FY 2019-2020 was 3.202 million metric tons (1.346 million metric tons + 1.856 million metric tons) and among these, the volume of fabric that was manufactured in the dyeing facilities of Bangladesh textile sector was 2.38 million metric ton (1.346 million metric ton + 1.034 million metric ton). Figure 10 represents the apparel export volume in million metric tons from 2007 to 2020

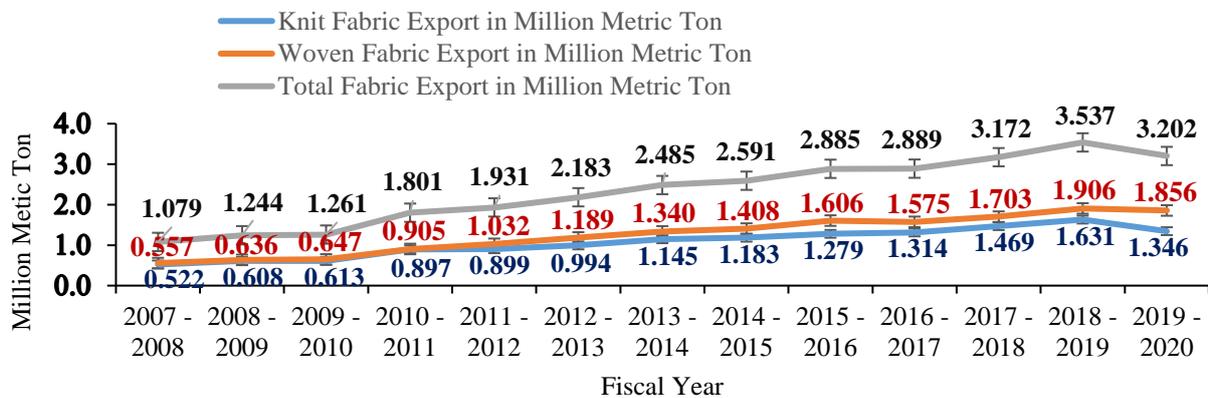


Figure 10. Annual apparel (knit and woven) export trend in Bangladesh (July 2007 – July 2020)

3.2 Textile Chemical Consumption

Bangladesh textile industry consumes vast quantities of basic and auxiliary textile chemicals. The basic chemicals include mainly caustic soda, sulphuric acid, hydrogen peroxide, calcium chloro-hypochlorite or bleaching powder, hydrochloric acid, etc. The auxiliary chemicals include different kinds of complex organic chemicals such as detergents, wetting agents, sequestering agents, anti-creasing agents, levelling agents, post-dyeing treatment chemicals - like soaping and softeners to improve product quality. Besides, fundamental, and auxiliary chemicals such as decolor ants, polymers, coagulants, salts and acids are used in Effluent Treatment Plants (ETP). The chemical consumption varies depending upon yarn count, fabric width, fabric gram per square meter (gsm), product aesthetic design or color, machine efficiency i.e., liquor ratio used in the dyeing machine. The consumption of dyestuffs and chemicals vary from industry to industry depending on the types of fabrics they manufacture.

Woven and denim dyeing processes require 10%-20% of additional chemicals with respect to knit dyeing process. The textile dyeing industry uses a wide range of chemicals, each intended to attain a specific purpose in wet processing. The type of chemicals, their functionality and usage in terms of per unit apparel (per kg of fabric) in wet processing sectors are represented in Table 3.

Table 3: Chemical wise breakdown of textile chemical consumption to produce per kg fabric

Sl No.	Type of Chemical	Functionality	Knit dyeing (gram/kg)	Woven dyeing (gram/kg)	Denim dyeing (gram/kg)	Yarn dyeing (gram/kg)
1.	Sizing agent	Increasing yarn strength	n/a	16-20	16-20	n/a
2.	Wax	Reduce surface tension,	n/a	0.75 - 1	0.75-1	n/a
3.	Wetting agent	influence rate of absorption	n/a	30-40	35-40	6-10

4.	Anti-foaming agent	Prevent foam formation	0-8	3-6	3-6	0-10
5.	Anti-creasing agent	Prevent crease mark formation on fabric	6-48	n/a	n/a	n/a
6.	Detergent	Remove suspended materials	3-7	2-4	0.3-1	6-10
7.	Sequestering/Demineralizing agent	Demineralize scouring/dyeing bath, removes hardness,	6-30	15-25	1.5-2.5	8-16
8.	De-aerating agent	deactivate metal ions	n/a	n/a	20-25	6-10
9.	Tri-sodium phosphate			0.7-1.2	n/a	n/a
10.	Stabilizer		0.7-7	2-6	n/a	n/a
11.	Sodium sulfate			3-6	n/a	n/a
12.	Enzyme (for enzymatic de-sizing)	Remove protruding fibres from surface		10-15	n/a	n/a
	Enzyme		1-5	n/a	n/a	n/a
	Caustic soda		6-18			10-14
	Caustic soda (with mercerizing)	Maintains color depth depending on fabric thickness	n/a	220-300	n/a	n/a
13.	Caustic soda (for sulphur rope dyeing)		n/a	n/a	180-250	n/a
	Caustic soda (for indigo dyeing)		n/a	n/a	150-220	n/a
	Hydrogen per oxide	Remove natural color of cotton fabric and for better absorption of dyes.	6-45	25-30		20-28
14.	Hydrogen per oxide (For sulphur rope dyeing)		n/a	n/a	12-18	n/a
15.	Brightening agent	Brighten white fabric	1-9	1-9		1-9
16.	Soda ash	Accelerate exhaustion process	30-100	60-100	0.2-0.4	70-120
17.	Glauber salt		100-500	150-250	n/a	250-450
	Acetic acid	Neutralization at different stages of dye bath	5-20	8-15	n/a	10-18
18.	Acetic acid (for sulphur rope dyeing)		n/a	n/a	15-25	n/a
	Acetic acid (for indigo dyeing)		n/a	n/a	8-15	n/a
19.	Hydrose	Use as reducing agent	6-18	n/a	25-30	8-24
20.	Hydrogen peroxide killing agent (Oxidizing agent)	Remove excess peroxide from dye bath	1-3	n/a	n/a	n/a
21.	Levelling agent (Cotton)	Ensure level dyeing	6-12	4-8	4-8	10-24
22.	Soaping agent	Remove unfixed dye from fabric surface	1-10	0.5-2.5	n/a	8-16
23.	Fixing agent	Fix unfixed dye on fabric	3-6	3-6	25-30	n/a
24.	Dispersing agent	Aggregate dispersed dyestuff	6-12	6-12	6-12	8-24
25.	Reducing agent	Strip dye from fabric	6-18	0.8-1.2	n/a	n/a
26.	Softening agent	Soften the fabric surface and make fabric more comfortable to wear.	5-10	6-12	15-18	n/a

3.3 Annual Textile Chemical Consumption

Material balance analysis was conducted to calculate annual textile chemical consumption based on product wise total textile chemical consumption of the dyeing industries. The calculations were carried out based on certain specific assumptions, such as printing process has been 30% of the annual knit fabric production, 40% of annual woven fabric production and Garment washing was 8% of annual knit fabric production. From the calculations it was found that the annual chemical consumption in the textile sector of Bangladesh in FY 2019-2020 was 1.757 million metric tons. Table 4 represents annual textile fabric production and chemical consumption in Bangladesh for FY 2019-2020.

Table 4. Annual Textile Fabric Production and Chemical Consumption in Bangladesh (FY 2019-20)

Parameter	Fabric Production in Million Metric ton	Fabric colored in Million Metric ton (P)	Chemical Consumed to produce per kg fabric in kg (C)	Total Annual Chemical Consumption in Million Metric ton, [T = P x C]
Knit Dyeing	1.000	1.345	0.500	0.500
Yarn Dyeing/Sweater	0.345		0.575	0.199
Woven Dyeing	0.977	1.034	0.875	0.855
Denim Dyeing	0.057		0.370	0.021
Printing (30% of Knit Fabric Production)		0.300		0.075
Printing (40% of woven Production)	n/a	0.391	0.250	0.098
Garments Washing (8% of Knit Production)		0.080	0.125	0.010
Total	2.379			1.757

Figure 11. depicts textile annual production and chemical consumption trend in textile industries from 2007 to 2020, derived from Eqn 1, 2 and 3. The graph indicates the increasing demand of textile chemicals, although the volume decreased in FY 2019-20 due to nationwide lockdown imposed since the outbreak of COVID-19 pandemic. Local chemical industries of Bangladesh produce basic chemicals which are consumed by the textile industries. But for dyestuff, auxiliaries and other chemicals, this sector is still largely dependent on chemical import.

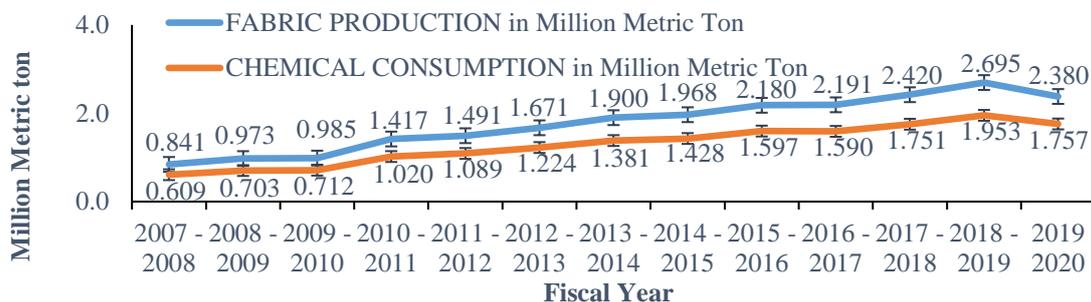


Figure 11. Textile chemical consumption trend with respect to annual production in Bangladesh (July 2007 – July 2020)

4. Economic aspects of textile chemical consumption

Sustainable chemical consumption the key to growth and competitiveness of Bangladesh textile dyeing sector. The competitiveness of Bangladesh's textile sector is impacted by an inadequate domestic supply of textile chemicals. Implementation of sustainable options in the textile production play key roles in continuous economic growth of the sector. The idea of resource efficiency regarding textile chemical production is a fundamental element of sustainable consumption. It can reduce the import dependency of basic and auxiliary chemicals. Figure 12 represents the textile chemical market value trend in Bangladesh from 2007 to 2020. These values were estimated using Eqn. 5.

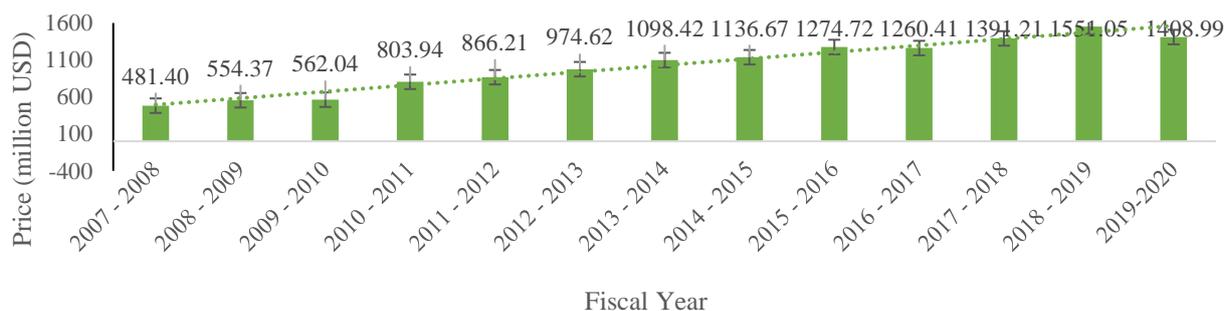


Figure 12. Textile chemical market value trend in Bangladesh (FY: July 2007 – July 2020)

Textile chemical consumption in Bangladesh had been estimated at around 1408.99 million USD in fiscal year 2019-2020. It is evident that the consumption decreased in FY2019-20 due to COVID-19 outbreak, but the trend of chemical market value presented in figure 12 indicates that the demand for textile chemicals will keep increasing in the future. At present, a limited number of the manufacturers produce chemicals in Bangladesh. These are mainly bleaching powder, caustic soda, hydrochloric acid, hydrogen peroxide, liquid chlorine, paraffin wax, sodium hypochlorite, and sulphuric acid. Among these, only caustic soda, hydrogen peroxide and sulphuric acid are used in textile dyeing industries. Figure 13 represents market value trend of mostly used textile chemicals in Bangladesh from July 2015 – July 2020.

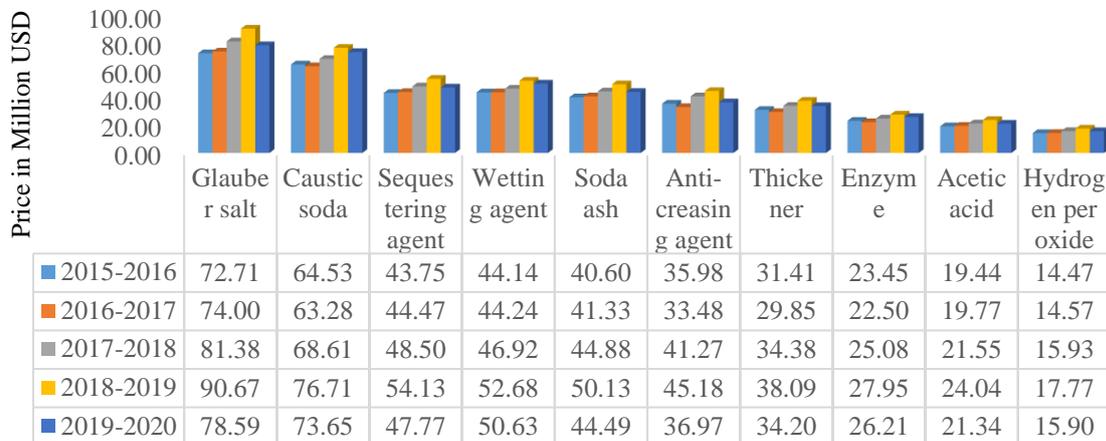


Figure 13: Market value of top ten textile chemicals consumed in Bangladesh (FY: July 2015 – July 2020)

Considering the huge volume of chemicals consumed in a fiscal year, manufacturing textile chemicals can be a futuristic business tool for Bangladesh. It may also empower sustainable textile production by improving the overall business ecosystem. Figure 14 depicts the quantity of top ten textile chemicals based on demand that has been consumed in Bangladesh textile sector in FY 2019-20.

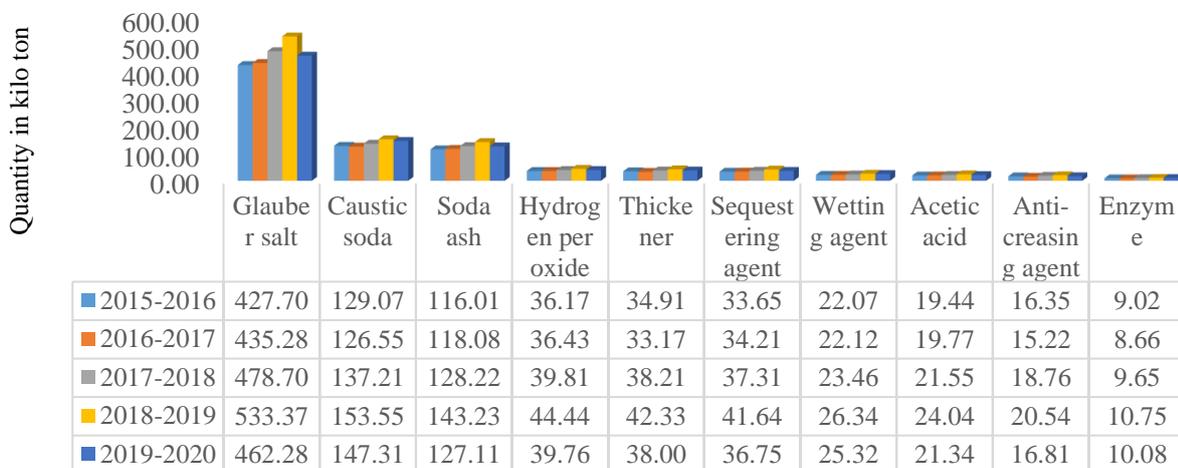


Figure 14: Quantity wise of top ten textile chemical requirement in Bangladesh (FY: July 2015 – July 2020)

5. Conclusion

This study demonstrates the amount of chemicals consumed in Bangladesh textile sector in a fiscal year. It had been calculated that 1.75 million metric ton of chemicals have been consumed to produce 2.38 million metric fabrics in FY 2019-20. More than 90% of the chemicals that are being used in the wet processing units of textile industries are imported. Hence, this bears a noteworthy impact on the economy of Bangladesh. The yearly expenses of chemical import are on the rise. In the post COVID-19 time, the price hike of chemicals is imminent. Therefore, it is important for Bangladesh to look for alternative options of chemical import. One option of substituting chemical import is formulation of chemicals within the country. But the local capacity is not yet developed. Moreover, the recent drive for sustainability involving chemical safety and security has been instigating changes in the chemical management system of the textile industries. This methodological study can help factory management to maintain chemical traceability starting from procurement to disposal. This article can also contribute to explore advanced traceability options and address live inventory management systems by helping factories to calculate their annual chemical consumption using the material balance audit tool. This will also help to identify the total life cycle of the chemicals used in wet processing. This study may also help the sectoral

stakeholders to identify the amount of chemicals consumed and procured in textile industries in a fiscal year, analyze the market of regularly consumed textile chemicals within the country and plan for formulation of chemicals within the country by enhancing local capacity. In addition, the mathematical tool used in this study may be implicated to prepare relevant databases of chemical consuming industries of Bangladesh.

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Supplementary Material

Appendix A1: Apparel Items Exported from Bangladesh
Table A1. Apparel Items Exported from Bangladesh (FY: 2019-2020)

Items	Price (Million US\$)	Percentage (%)
Shirts	1,783.14	6.38
Trousers	5,447.13	19.49
Jackets	3,514.21	12.57
T-Shirt	5,614.00	20.09
Sweater	3,597.68	12.87
Estimated Denim	2,161.30	7.73
Knit apparel (others)	4,696.32	16.80
Woven apparel (others)	1,135.41	4.06
Total Apparel	27,949.19	100.00

Appendix A2: Item wise average product weight and export price in USD
Table A2. Average item wise product weight and export price in USD

Product Items	Child's + Men's + Women's per piece product weight		Average weight of per piece product	Export Price in USD		Average Price in USD
	Minimum	Maximum		Minimum	Maximum	
T-Shirt	130	230	180	1.50	3.50	2.50
Sweater	220	380	300	2.50	5.00	3.75
Shirt	180	320	250	1.50	5.00	3.25
Trouser (Knit + Woven)	250	350	300	2.00	5.00	3.50
Denim	200	400	300	1.50	5.00	3.25
Jacket/Coat	300	500	400	2.50	5.00	3.75
Knit Other's Product Item						
Sock's	50	150	100	0.40	1.00	0.70
Knit women's suit's	180	360	270	2.20	4.50	3.35
Outfit	180	360	270	2.20	4.50	3.35
Underpants	60	150	105	0.40	1.20	0.80
Leggings	150	220	185	1.50	3.50	2.50
Hat (knit)	120	220	170	1.00	2.00	1.50
Gloves	60	220	140	0.50	2.00	1.25
Knit Babies garments	100	300	200	1.50	3.20	2.35
Swimming suit	60	120	90	0.60	1.50	1.05
Lingerie	40	100	70	0.50	0.80	0.65
Average per piece other's knit item product weight			160	Average per piece other's knit item product price		1.75
Woven Other's Product Item						
Gabardine	200	360	280	1.75	3.50	2.63
Shorts	80	200	140	0.50	1.75	1.13
Outfits	150	360	255	2.00	3.50	2.75
Anoraks	130	320	225	1.50	3.00	2.25
Tops & Lingerie	60	180	120	0.50	0.80	0.65
Skirt	200	350	275	2.00	2.50	2.25
Brassieres	50	160	105	0.50	0.75	0.63
Average per piece other's woven item product weight			200	Average per piece other's woven item product price		1.75

Appendix A3:

Table A3. Apparel items exported from Bangladesh textile industry [5]

Year	Type of Apparel: Knit (Export value in million USD)			Total Knit Apparel Export value in million USD	Type of Apparel: Woven (Export value in million USD)					Total woven Apparel Export value in million USD
	T-Shirt	Others	Sweater		Shirts	Trousers	Jackets	Others	Denim	
2006-2007	2208.90	1096.61	1248.09	4553.60	943.44	2201.32	1005.06	132.81	375.00	4657.63
2007-2008	2765.56	1292.87	1474.09	5532.52	915.60	2512.74	1181.52	200.00	300.00	5167.28
2008-2009	3065.86	1504.78	1858.62	6429.26	1000.16	3007.29	1299.74	200.00	300.00	5918.51
2009-2010	3145.52	1542.38	1795.39	6483.29	993.41	3035.35	1350.43	159.24	475.00	6013.43
2010-2011	4696.57	2297.30	2488.19	9482.06	1566.42	4164.16	1887.50	200.00	300.00	8432.40
2011-2012	4713.11	2432.94	2340.34	9486.39	1733.54	4686.39	2231.16	202.25	750.00	9603.34
2012-2013	5143.22	2711.93	2620.73	10475.88	1972.89	5185.48	2634.28	247.20	1000.00	11039.85
2013-2014	5863.81	3253.06	2932.94	12049.81	2173.73	5690.78	2973.16	238.95	1365.45	12442.07
2014-2015	6064.13	3533.50	2829.16	12426.79	2271.43	5697.83	3183.17	235.73	1676.45	13064.61
2015-2016	6118.53	4054.42	3182.47	13355.42	2317.09	6319.00	3774.08	588.84	1739.73	14738.74
2016-2017	5861.98	3639.81	3361.53	13757.25	2108.38	6026.69	3546.88	817.11	1893.53	14392.59
2017-2018	6292.25	5221.56	3674.70	15188.51	2063.57	6389.38	3978.47	1439.48	1986.94	15426.25
2018-2019	7011.26	5621.37	4255.91	16888.54	2324.85	6939.61	4384.81	1379.07	2216.39	17244.73
2019-2020	5614.00	4696.32	3597.68	13908.00	1783.14	5447.13	3514.21	1135.41	2161.30	14041.19

Here, Knit apparel export value (others) = Total knit apparel export value: (T-Shirt + Sweater) and, other Woven apparel export value = Total woven apparel export value: (Shirt + Trouser + Jacket + Denim).

Appendix A4

Table A4. Process wise Monthly Production and Chemical Consumption Report of Textile dyeing factory [Fiscal Year 2019–2020]

Month	Knit dyeing industries annual report			Yarn dyeing industries annual report		
	Knit dyeing production (kg)	Total dyestuff + chemical consumption (kg)	Average chemical consumption in kg/kg	Yarn dyeing production (kg)	Total dyestuff + chemical (kg)	Average chemical consumption in kg/kg
July	229617	120286.262	0.524	349509	213134.339	0.610
August	301001	164640.803	0.547	339796	196113.654	0.577
September	230277	119887.949	0.521	319727	181476.871	0.568
October	300615	136596.281	0.454	358417	193395.127	0.540
November	350759	145352.503	0.414	398575	221971.301	0.557
December	318448	139926.945	0.439	384179	218608.657	0.569
January	267977	142885.157	0.533	332769	183896.751	0.553
February	247515	135652.815	0.548	328881	176920.516	0.538
March	328588	151581.053	0.461	376136	208674.652	0.555
April	351912	171951.303	0.489	389293	225199.985	0.578
May	438068	233082.079	0.532	399667	257218.293	0.644
June	274452	146835.142	0.535	364615	224571.442	0.616
Average Chemical Required in kg to produce per kg knit fabric			0.500	Average Chemical Required in kg to produce per kg knit fabric		0.575
Information for Knit dyeing industry: Liquor to fabric weight ratio: 1:6 (Normally varies 1:6~8); Dyeing capacity: The average per day dyeing capacity of the industry is 12 ~ 14 tons of knit fabric.				Information for yarn dyeing industry: Liquor to fabric weight ratio: 1:8. Dyeing capacity: The average per day dyeing capacity of the industry is 13 ~ 14.5 tons of yarn dyed fabric.		
Month	Woven Dyeing Industries Annual Report			Denim Dyeing Industries Annual Report		
	Production (kg)	Total Dyestuff + Chemical Consumption (kg)	Average Chemical Consumption in kg/kg	Production (kg)	Total Dyestuff + Chemical Consumption (kg)	Average Chemical Consumption in kg/kg
July	122763.344	121879.805	0.993	897217.2274	344968.061	0.384
August	120838.646	110159.144	0.912	816495.218	297974.305	0.365
September	129136.573	101513.942	0.786	699732.1341	249134.332	0.356
October	146833.821	138068.693	0.940	692815.771	241967.350	0.349
November	158654.606	127603.187	0.804	746408.6652	269356.125	0.361
December	183119.799	144576.547	0.790	693195.3893	259622.690	0.375
January	192852.104	147631.702	0.766	677792.863	264125.805	0.390
February	131346.131	125106.500	0.952	642979.2652	247151.772	0.384
March	121600.227	138749.776	1.141	670794.437	258926.653	0.386
April	175862.437	146701.107	0.834	717724.9223	264563.540	0.369
May	192701.777	144411.604	0.749	780576.4079	286471.542	0.367

June	105648.792	87412.597	0.827	1012340.713	356776.300	0.352
Average Chemical Required in kg to produce per kg woven fabric			0.875	Average Chemical Required in kg to produce per kg denim fabric		0.370
Information woven and denim dyeing industry: Monthly production of woven and denim industry generally stands at yard, so the values were converted to kg using following formula. Production Meter to Kg conversion formula: Production (kg) = [Production(meter) x GSM x Dia. (meter)] /1000 Assumption: GSM of woven = 250 and dia. Of woven fabric = 1.5 meter and GSM of denim fabric = 250 (generally lies between 4 ~ 15 ounce) and denim fabric dia. = 1.46 meter. Dyeing capacity: The average per day dyeing capacity of the woven industry is 5.5 ~ 7 tons of and denim industry is 28 ~ 30 tons.						
Month	Print (Knit + woven) Dyeing Industries Annual Report			Garments Washing Industries Annual Report		
	Production (kg)	Total Dyestuff + Chemical Consumption (kg)	Average Chemical Consumption in kg/kg	Production (kg)	Total Dyestuff + Chemical Consumption (kg)	Average Chemical Consumption in kg/kg
July	77665	17917.761	0.231	4937	584	0.118
August	93024	21277.222	0.229	3596	494	0.137
September	117679	33490.983	0.285	4800	587	0.122
October	163129	38237.847	0.234	5334	621	0.116
November	204650	50838.342	0.248	4798	579	0.121
December	199111	51987.222	0.261	3850	535	0.139
January	187679	47098.985	0.251	3996	544	0.136
February	133129	38287.817	0.288	4929	617	0.125
March	173129	42267.347	0.244	4992	585	0.117
April	154650	40838.162	0.264	5584	593	0.106
May	194650	37838.142	0.194	4636	549	0.118
June	173764	47917.761	0.276	4121	566	0.137
Average Chemical Required in kg to produce per kg printed fabric			0.250	Average Chemical Required in kg to produce per kg garments washing fabric		0.125
Information for printing and garments washing industry: The average per day printed capacity of the industry is 5.5-6.5 tons and garments washing industry is 175-200 kg of fabric						

Appendix A5

Table A5. Process wise average chemical consumption to produce per kg fabric

Types of dyed fabric		Average chemical consumption (gram)
Knit dyed fabric (basic)		500
Knit dyed fabric	White Color	50-150
	Light Color	150-450
	Medium/Dark Color	450-650
	Extra Dark Color	650-800
	Black Color	400-750
	Double Part	300-800
	100 % Polyester	80-200
Yarn dyed fabric		575
Woven dyed fabric		875
Denim dyed fabric		370
Printed dyed fabric		250
Garments washed fabric		125

Appendix A6: Annual textile chemical consumption and market value analysis: July 2019 – July, 2020)

Here, Total fabric production in million metric ton (P) = Knit dyed (P_k) = 1.223, woven dyed (P_w) = 1.007, denim dyed (P_d) = 0.057, yarn dyed (P_y) = 0.408, knit printed (P_k) = 0.366, woven printed (P_w) = 0.402, garments washing (P_g) = 0.097..

Table A6: Breakdown of annual textile chemical consumption and market value analysis

Sl No.	Chemicals	Average Chemical Consumed for per kg fabric in gram Q	Average Per Kg Chemical Price in USD, f	Chemical Consumption Percentage (based on annual Production), W	Chemical Consumption of knit dyeing industries in kilo ton, a= ($P_k \times Q \times W$)	Chemical Consumption of woven dyeing industries in kilo ton, b = ($P_w \times Q \times W$)	Chemical Consumption of denim dyeing industries in kilo ton, c= ($P_d \times Q \times W$)	Chemical Consumption of yarn dyeing industries in kilo ton, d= ($P_y \times Q \times W$)	Total annual chemical consumption in kilo ton, (s = a+b+c+d)	Annual Chemical Market Value in million USD. (f × s)
1.	Sizing Agent	18	0.90	45%		7.91	0.46		8.38	7.54
2.	Wax	0.875	0.70			0.38	0.02	-	0.41	0.29
3.	Anti-foaming Agent	4.5	3.25	10%	0.45	0.44	0.03	0.16	1.07	3.48
4.	Anti-Creasing Agent	24	2.20	70%	16.81				16.81	36.97
5.	Wetting Agent	32	2.00	70%		21.89			25.32	50.63
		37.5				1.50				
		8					1.93			
6.	Detergent	3	1.80	75%	2.25	2.20			6.55	11.79
		8						2.07		
6.	Detergent (Sulphur rope dyeing)	0.65					0.03			
7.	Sequestering agent	18	1.30	80%	14.40				36.75	47.77
		20				15.63				
		24						6.63		
		2		70%			0.08			
8.		8	1.00	75%				2.07	2.52	2.52

	De-Aerating agent	22.5		35%			0.45			
9.	Tri-sodium phosphate	0.95	0.40	70%		0.65			0.65	0.26
10.	Stabilizer	2.25	1.50	80%	1.80				7.66	11.49
		4				5.86				
11.	Sodium Sulfate	4.5	0.01	75%		3.30			3.30	0.03
12.	Enzyme	2.5	3.2	75%	1.88				10.08	32.25
	Enzyme (with enzymatic de-sizing)	14		60%		8.21				
13.	Caustic soda	9	0.50	85%	7.65				147.31	73.65
		12						3.52		
	Caustic soda (with mercerizing)	260		50%		127.01				
	Caustic soda (sulphur rope dyeing)	215		40%			4.90			
Caustic soda (indigo dyeing)	185				4.22					
14.	Hydrogen per oxide	18	0.40	75%	13.50				39.76	15.90
		27.5				20.15				
		24		70%				5.80		
	Hydrogen per oxide (sulphur rope dyeing)	15		35%			0.30			
15.	Brightening Agent	5	2.75	10%	0.50	0.49		0.17	1.16	3.19

16.	Acetic acid	10	1.00	80%	8.00				21.34	21.34
		11.5				8.99		.		
		14						3.63		
	Acetic acid (Sulphur rope dyeing)	20		40%				0.46		
Acetic acid (Indigo dyeing)	11.5						0.26			
17.	H ₂ O ₂ killing agent	1.5	1.00	80%	1.20				1.20	1.20
18.	Levelling agent - cotton	9	1.40	75%	6.75			2.33	13.74	19.23
		6				4.40	0.26			
19.	Levelling agent – polyester	6	2.20	10%	0.60	0.59	0.03	0.21	1.43	3.14
20.	Soda ash	65	0.35	70%	45.51				127.11	44.49
		80		75%		58.62				
		95		70%				22.97		
		0.3		65%			0.01			
21.	Glauber salt	300	0.17	75%	225.07				462.28	78.59
		200				146.55				
		350						90.66		
22.	Sodium sulfide	2	0.35	65%			0.07		0.07	0.03
23.	Soaping agent	5.5	1.90	65%	3.58				7.37	14.00
		1.5		75%		1.10				
		12		65%				2.69		
24.	Reducing agent	12	2.25	5%	0.60				0.70	1.57
		1		10%		0.10				
25.	Fixing agent - color (Cotton)	4.5	2.00	50%	2.25	2.20			4.92	9.84
		27.5		30%			0.47			
26.	Fixing Agent -	4.5		10%	0.45	0.44			0.89	1.78

	white (Cotton)									
27.	Fixing Agent - Color (Polyester)	3.5		8%	0.28	0.27		0.10	0.88	1.76
		40		10%			0.23			
28.	Softener – Color (Cotton)	7.5	1.60	55%	4.13			1.42	10.62	16.99
		9				4.84				
		13.5		30%			0.23			
29.	Softener - White (Cotton)	7.5		10%	0.75			0.26	1.94	3.10
		9				0.88	0.05			
30.	Dispersing agent	16	1.50	10%				0.55	2.33	3.50
		9			0.90	0.88				
31.	Hydrose	27.5	1.20	60%				0.94	3.73	4.47
		12		10%	1.20	1.17		0.41		
32.	* Others (dyestuff + auxiliaries and ETP chemicals)	-	1.2		139.64	409.75	6.09	50.99	606.48	727.77
Total (knit + woven + denim + yarn)					500.15	854.90	21.09	198.59	1574.73	1244.54
34	Thickener (Printing)	100	0.90	55%	16.50	21.49			38.00	34.20
35	* Printing others (Chemical + dyestuff + pigment)					58.52	76.21			134.73
Total (printing)					75.02	97.70			172.73	155.45
Garments washing (other)			0.75		10.00				10.00	9.00
Total (knit + woven + denim + yarn + print + washing)									1757.46	1408.99

Design And Development of An Open-Source and Affordable IoT System for a Wide Array of Industrial and Domestic Applications

Anindya Karmaker, Mahmudul Hasan, and Ahaduzzaman Nahid*

Department of Chemical Engineering, Bangladesh University of Engineering and Technology (BUET),
Dhaka, Bangladesh

Received: 5 September 2022; Accepted: 19 October 2022; Published: 30 April 2023

Abstract: The Internet of Things (IoT) has improved the quality of our lives through various interconnected gadgets and devices. Despite having great potential, IoT systems still have not made it into the mainstream industries or residential complexes due to the high cost associated with commercial IoT solutions particularly in developing or least developed countries. In-expensive and open-source IoT-based systems could be employed in these fields to improve overall safety and drastically reduce accidents. In this paper, a model IoT system has been presented that could be used in any commercial apartment or building complex or retrofitted to existing industry and can augment safety and reliability along with improving the quality of life. For this purpose, Atmega1284P and ESP32 microcontroller-based IoT device was developed and implemented. For IoT integration and cloud operation, the Google Firebase IoT platform was chosen. To monitor the system using both Bluetooth (low energy, BLE) and Wi-Fi, an Android application was created using MIT App Inventor 2. This device is capable of receiving and handling multiple analog or digital sensors and will send an automated email whenever a threshold value for the sensor is exceeded which could be easily changed via the application. Furthermore, the delay and system response of this device were experimentally determined. This type of system could be easily scaled for various applications which are also discussed in this paper. It also offers better flexibility and cost-effective solution to commercially available alternatives.

Keywords: *IoT, ESP32, Atmega1284P, Firebase, Industrial Safety, Automated email response*

1. Introduction

The Internet of Things (IoT) is a network of physical objects embedded with sensors, software, and other technologies to connect and exchange data with other devices or systems over the internet[1]. IoT has taken the modern technological world by storm[2] and is omnipresent in our day-to-day lives. From smart sensors to smart cars, these devices are improving people's lives and making them easier and safer[3], [4]. However, these systems are still not being used to their full extent since they are very expensive. Almost every day in many industries and residential complexes, various accidents are occurring. These accidents could easily be prevented if there were automatic response systems instead of age-old systems that rely on human intervention. For instance, fire hazard is one of the major causes of accidents in developing and least-developed countries[5]. Electrical short circuits and gas leakage are two of the most common causes of fire hazards. However, despite the presence of cheap gas leakage detectors or fire alarms, many accidents could not be prevented since they require some form of human interaction, which is time-consuming and consequently increases the damage. Some industries and apartments do not even have gas detectors, smoke, or fire alarms to alert employees in case of an accident. Those that do have such systems are mostly manually operated, and hence fail to serve their purpose if no one is present on-site to monitor them. Moreover, various small industries in developing countries do not usually require sophisticated control systems, and sometimes they do not even have the capital to invest in modern control and monitoring systems like DCS (distributed control system) or SCADA (supervisory control and data acquisition)[6]. Though there are some inexpensive but sophisticated IoT monitoring systems available nowadays, they are quite unstable for 24x7 operation and have cheap components with closed source software. Some commercial IoT systems employ a special watchdog service for added reliability but charge a premium for added features[7]. There has been a lot of research into developing inexpensive IoT solutions for developing countries, however, they use new cloud platforms or LoRa based systems[8], [9]. In this paper, a model IoT system has been presented which has several analog and digital sensors and costs less than 100 USD. This system uses traditional communication systems like Wi-Fi and Bluetooth but could also be adapted for LoRa operation. Since this system is built from scratch, it is possible to choose the best components required and adjust the costing appropriately. A detailed framework and flowchart of the design and working process are explained in this paper for a better understanding of this system so that anyone can build it using this system as a reference. The major advantage of this system is that it can provide real-time monitoring of important process variables with an automated response system to alert the user or emergency response services in case of an accident as early as possible to minimize the loss of lives and damage of property. An authorized user can monitor this system from anywhere in the world using an internet connection. This system could be scaled as required and due to the open-source nature of this system, it could be improved or modified without needing expensive licensing permission. This system can also control other devices (via infrared), like turning on the exhaust fan or an appliance as required which is a useful feature not present in even some of the commercial solutions. To summarize, industrial and residential development in developing and least-developed countries are occurring at an unprecedented rate. However, the number of accidents is also increasing proportionally. This project aims to reduce avoidable accidents by warning and alerting the people beforehand, and at least keep the damage to a minimum with the least investment cost.

* Corresponding Author: Ahaduzzaman Nahid,
E-mail: ahaduzzaman@che.buet.ac.bd

2. Instrumentation and Design

Design: The IoT system consisted of two independent microcontroller circuits. One of the systems was powered by Atmega1284P, which houses various ADCs (analog to digital converter) and is called the sensor hub for referencing purposes. The microcontroller received input from an RTC module DS3231 to maintain accurate timing, a thermocouple amplifier MAX31855, an RTD-to-digital converter MAX31865, a 40 kHz infrared receiver TSOP31240, and a 16-bit ADC ADS1115. Analog sensors were connected to the ADC, which was operated in single-ended input channel mode. The analog sensors consisted of temperature sensor LM35, gas sensor MQ2, and an analog pH sensor. RCWL-0516 Microwave proximity sensor was embedded into the circuit for monitoring or detecting people. A GPS module, NEO-M8N was also connected to the microcontroller along with four infrared LEDs and a buzzer. This microcontroller board was also connected to a Bluetooth low-energy (BLE) wireless serial module, HM-10.

The other microcontroller system was powered by ESP32. This board is referred to as the communication hub of the system. ESP32 was programmed to receive serial data from the sensor hub circuit and send the data to the Google cloud service, Firebase. The communication hub took less than 30 seconds to connect to the Wi-Fi network and the internet. In case the Wi-Fi network was unavailable, the hub was designed to create its Wi-Fi hotspot in less than 60 seconds. The user could connect to the hotspot and enter the Wi-Fi credentials manually or search nearby Wi-Fi networks and set it up for online operation. ESP32 was chosen due to its availability; however, it could be replaced by a lower-cost ESP8266 board to reduce the cost.

The sensor hub received sensor data from various amplifiers and ADC and transmitted the data via serial communication (UART) to both the BLE module and the communication hub and received serial data (UART) from both. The sensor hub circuit was coded to receive, save and transmit IR codes of devices like Fan, AC, or other IR-based relay modules to control those devices. The system also had a battery management system (BMS) using the conventional TP4056 module, which was modified so that the ADC could measure the battery voltage and give a warning if the BMS fails.

The system could be shifted to a single microcontroller board; however, multiple microcontrollers were used to ensure stable operation, easier serviceability, and maintenance. Both controllers operated in such a way that each could receive and transmit data independently and could be easily diagnosed if one or the other stopped working. Various modules like the GPS or ESP32 were powered using MOSFETS so that they could be turned off for debugging purposes or to reduce power consumption. The system could also be connected to a GSM shield directly so that it could operate without Wi-Fi or send critical information to the user via SMS.

Programming: Both microcontrollers were programmed using the Arduino Integrated Development Environment (IDE). Various libraries were used in the Arduino code, particularly IOXhop_FirebaseESP32, which was used to communicate ESP32 with Firebase. For thermocouple reading, RTD, and ADS1115, libraries from Adafruit were used. Moreover, SPI, Wire, Liquid Crystal, Software Serial, EEPROMAnything, TinyGPS++ by Mikal Hart, Wi-Fi Manager by Zhouhan, and IRremote library by Ken Shirriff were used. The mobile app interface was developed using the MIT App Inventor. The complete block diagram for the mobile application is presented in supplementary figures. Simplified block diagrams for the IoT device (both sensor hub and communication hub) are shown in Figures 1 and 2.

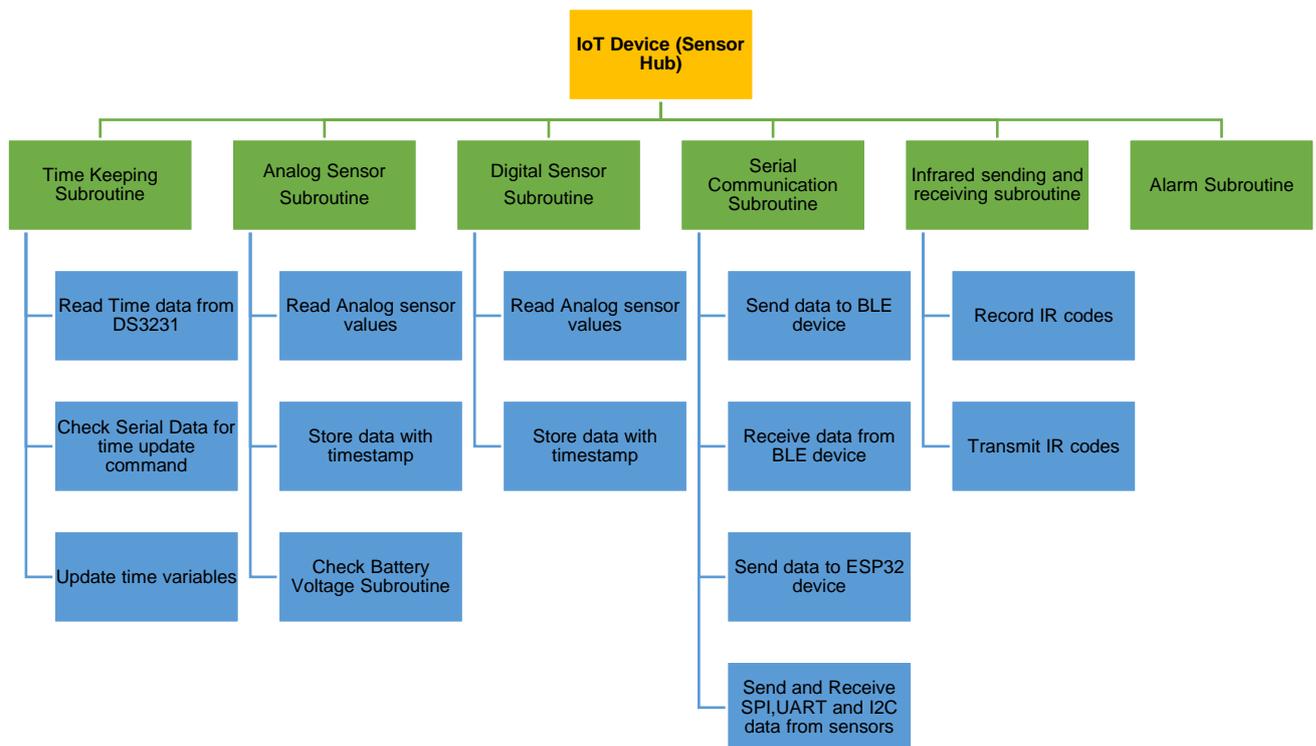


Figure 1: Simplified Block Diagram for Sensor Hub Circuit.

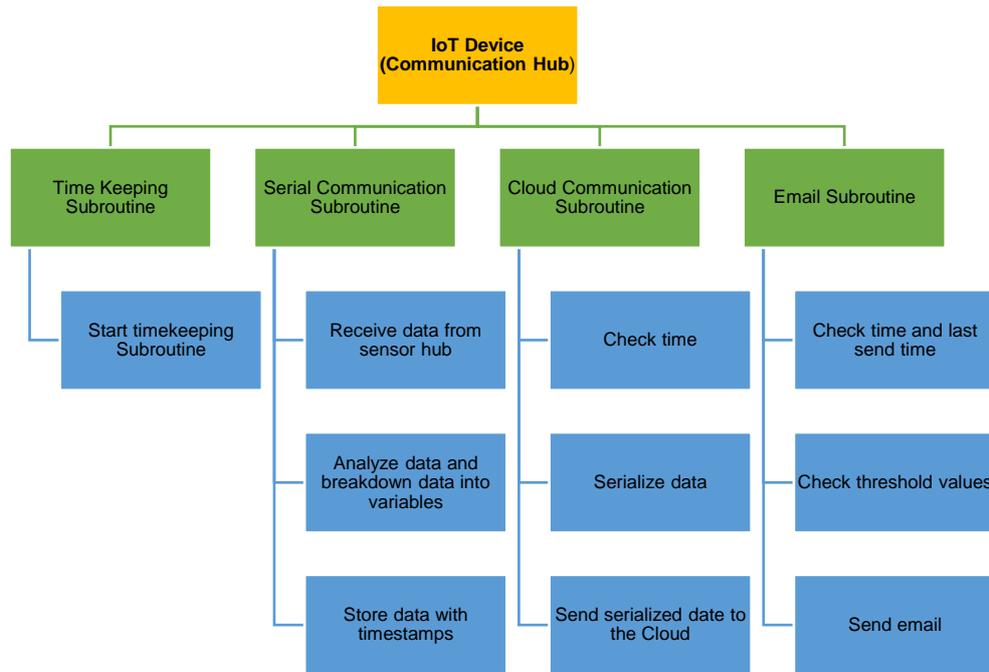


Figure 2: Simplified Block Diagram for Communication Hub Circuit.

From Figure 1, it can be observed that there were five important subroutines for the sensor hub circuit. The first one is the timekeeping subroutine. To accurately measure variables and average the readings, it was necessary to measure time accurately. DS3231 chip was used to measure time. It was connected via the I²C protocol. To update time, this subroutine regularly checked for the time update command received from the BLE device, like a mobile phone, using the developed application. The accurate time data was stored in variables for other purposes. Analog sensor subroutine checked for sensor value changes. It stored the data with timestamps. It also had a battery voltage measuring subroutine with an alarm function. It had several other subroutines to precisely measure temperature, pH, etc. Similarly, the digital sensor subroutine performed the same task. Serial communication subroutine sent and received data from various I²C, SPI, or UART sensors. It also stored values with timestamps. The infrared sending and receiving subroutine currently stores sensor values when the user enters the option using the device manually. It has several subroutines to decode and store the IR codes. It can also send the IR codes. However, the process of automatic sending of IR codes via Wi-Fi or based on the threshold values has not yet been implemented. The IR codes can be transmitted via the BLE commands using the mobile application. The alarm subroutine sends a signal to a piezoelectric buzzer to create a loud sound to warn the user if any subroutine sends the alarm command.

From Figure 2, it is observed that there were four important subroutines for the communication hub circuit. The timekeeping subroutine was similar to the sensor hub, however, the major difference was that it used the internal clock of ESP32. The serial communication subroutine also worked in a similar manner. It stored data with timestamps and broke down the data into variables for storage. Cloud communication subroutine checked time, serialized the data into proper formats, and finally sent the data to the Firebase Cloud server. Email subroutine was an important part of the communication hub circuit. It checked the time and stored them. It also compared the sensor values to the threshold values and sent them via email. To avoid spamming, it measured the time difference values and sent them after a regular interval.

Setup: The IoT system had a simple setup. The setup and operation process are illustrated in Figure 3. First, the device was powered on and connected to a 5V power source, the required sensors were connected and their values were monitored through the LCD on the device. The device created a hotspot Wi-Fi network. The user then connected to this hotspot and set up a Wi-Fi connection; ran the mobile application. A green Wi-Fi connection option indicated successfully connection of the device to the internet. To prevent unauthorized access and ensure security, device properties like threshold values and other feature selection options like GPS were activated when the device was connected via Bluetooth that was pin protected. The device then works autonomously and alerts the user or emergency services personnel based on the set threshold values.

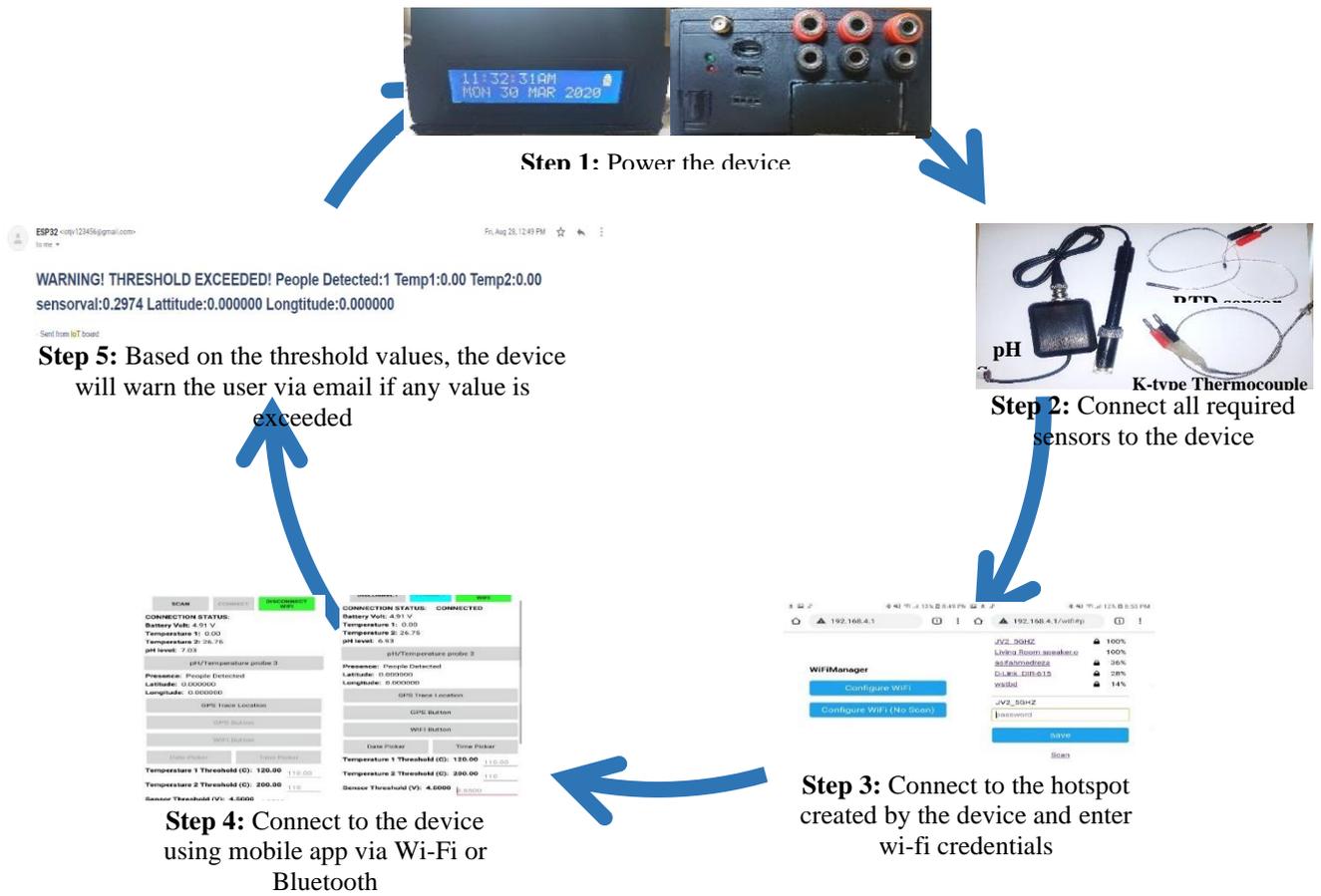


Figure 3: IoT device setup and working procedure.

3. Simulation and Results

Since the sensor hub circuit is complicated and has lots of components and libraries, the circuit was simulated in Proteus 8 Professional, to test how the various libraries would work together and be debugged as required. Using Proteus, the PCB was also designed and fabricated in-house. Atmega1284P was operated at 16MHz using an external crystal. The BLE and ESP32 modules were simulated using two terminals (UART communication). The thermocouple module was simulated using the MAX31855 module. The circuit diagram of the system is shown in Figure 4.

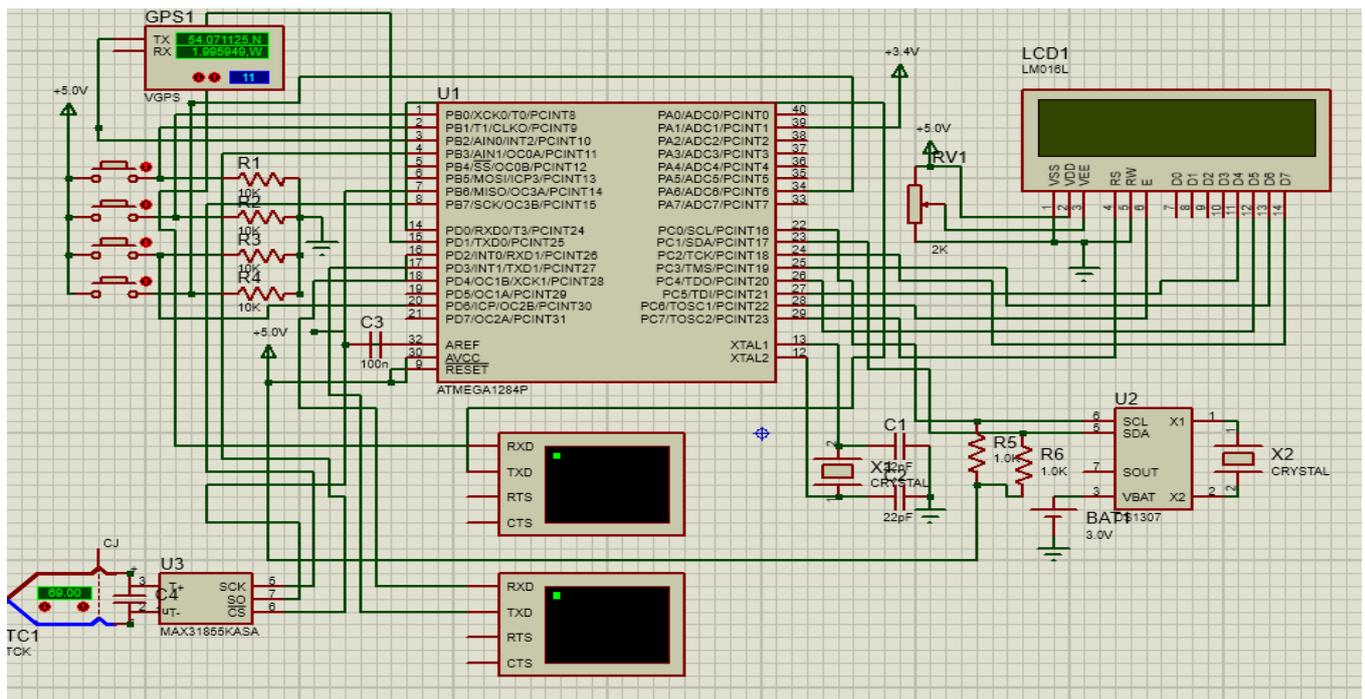


Figure 4: Simulation of sensor hub circuit.

The IoT system was also tested in lab condition to determine the delay and system response. During the testing, system lag, response lag, and accuracy were tested. Thermocouples, pH sensors, GPS sensors, and IR LEDs were tested during this process. Figure 5 and 6 compares the output data from the developed system taken using Wi-Fi and Bluetooth connection simultaneously and input data measured using locally connected sensor probes. This data was used to calculate the delay and evaluate system performance.

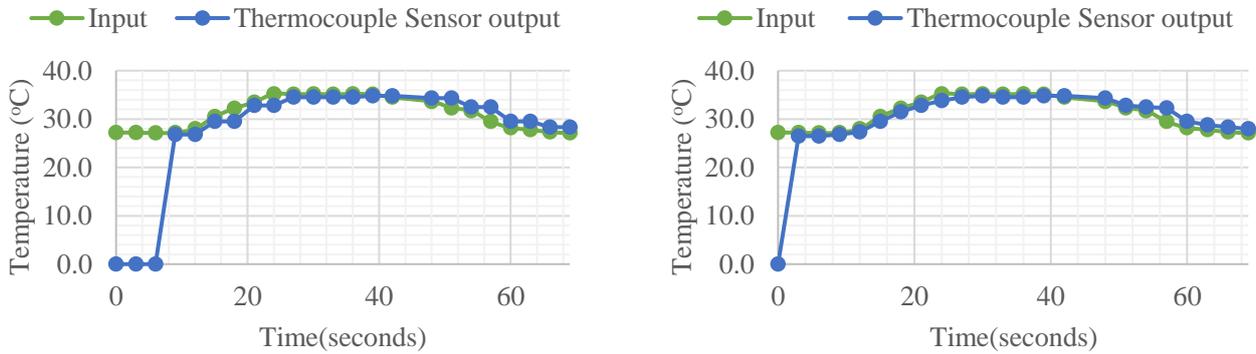


Figure 5: Temperature Input vs. Thermocouple Output on Wi-Fi connection(left) and Bluetooth (right).

A sample water bath with a temperature of $\sim 27^{\circ}\text{C}$ and pH of ~ 7.05 was used to determine the temperature and pH sensor accuracy and response lag. An RTD thermometer of 0.1°C accuracy was used for comparing the output from the IoT device and a benchtop pH meter was used to measure the pH. A water bath was heated and then cooled by adding hot and cold water and stirred continuously. The temperature was noted using both thermometer and IoT device. The readings were taken using both Bluetooth and Wi-Fi connection simultaneously at an interval of 3 seconds. There was an initial delay of 3 seconds for Bluetooth and ~ 6 seconds for Wi-Fi. The thermocouple sensor values varied within a margin of 0.5°C from the RTD thermometer. The response lag was roughly 1 second for the Bluetooth and about 6 seconds for the Wi-Fi though the initial response lag was 3 seconds and 6 seconds respectively for the Bluetooth and Wi-Fi. The same response lag was also observed from the pH sensor reading values as well.

The whole system was connected to the network and fully operational within 1 minute and 30 seconds after powering on. The sensors, particularly the GPS sensor took an average of 3 minutes to connect to the satellite and send accurate GPS coordinates within 10-meter accuracy without an external antenna. When the Wi-Fi was disconnected, the system warned the user in less than ~ 15 seconds. The battery backup system with 6000 mAh battery ran the system for an average of ~ 6 hours 32 minutes. All tests proved the reliability and effectiveness of this device in various industrial and residential apartment applications.

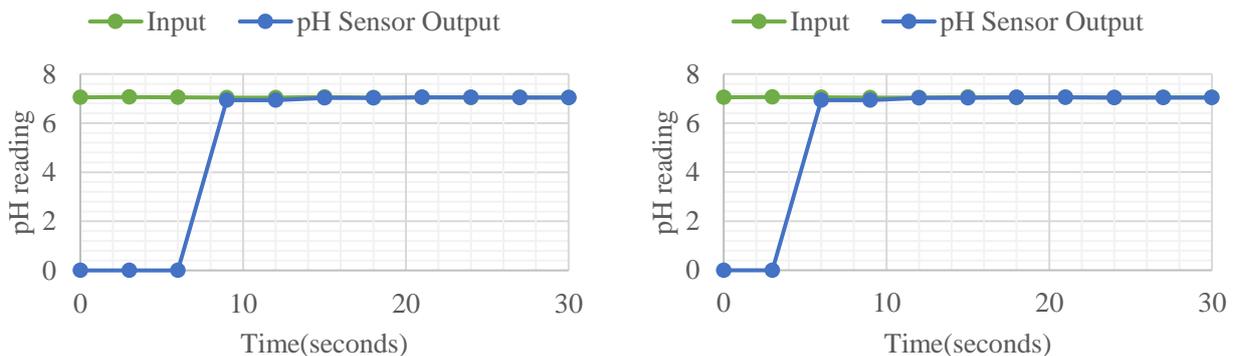


Figure 4: pH Input vs. pH Output on Wi-Fi connection(left) and Bluetooth (right).

4. Applications

This system has a lot of potential applications and therefore could be used in a variety of fields ranging from industry to healthcare. The potential applications of this system are listed below:

1) Industrial Applications: This type of device can be used to monitor non-process variables like electricity flow in the wiring, smoke detection, gas leakage detection, people detection and monitoring, etc. Since this device is inexpensive, both large and small-scale industries can adopt it and use it to improve reliability and safety. Moreover, improved security measures could be implemented in this system for better safety and reliability[10], [11].

2) Smart Home Applications: This IoT device is perfectly suitable for both small homes to large residential complexes[12]. If this device is present in every apartment then common accidents due to gas leakage or shortcircuit can

be easily prevented[13]. It can also monitor for intruders to prevent burglary. Moreover, since only a few sensors are needed, the cost is much lower compared to other market solutions.

3) Medical Applications: By connecting smart sensors such as SpO₂, heart rate, etc. to this IoT device the health condition of the patients can be monitored at home or hospitals and doctors can monitor a large number of patients quickly and easily[14], [15]. Moreover, an automated response can possibly prevent unnecessary deaths that usually occur due to negligence or systematic issues[16].

4) Agricultural Applications: This device can also be used for agricultural applications[17]. By monitoring soil water content, humidity, temperature, pH, etc. farmers can grow healthier crops easily[18]. Moreover, since all crucial parameters being measured can be sent to the agricultural specialists automatically, they can utilise the data to improvise crop growth and increase yield.

5) Water Management Applications: This device can be used to measure the water levels of ponds, lakes, wells, etc. by using various sensors[19], [20]. In addition, long-term water monitoring can signify drought early and appropriate measures can be taken quickly before the situation escalates.

In short, this type of open-source and inexpensive IoT design is useful and can be applied to various fields. From monitoring to preemptive decision making, this system offers a lot of advantages over commercial systems that are both expensive and closed-source in nature[21]. IoT has a lot of potential applications and it is time to utilize this technology in improving the safety and ease of monitoring in industries, hospitals, and houses.

5. Conclusions

Every year, thousands of people die, and millions of dollars are lost due to accidents in industries and households. IoT is not something new and is present in various gadgets and smart-home appliances that we use regularly. Using this developed IoT system, major accidents can be minimized and loss of lives can be prevented. This type of device with its low cost is perfectly suitable for developing countries where industrial and residential development is occurring rapidly, and an affordable solution is needed to prevent accidents and improve quality of life. The proposed IoT-based developed model will provide the groundwork for advanced IoT applications. Using the parameters obtained and the open-source code and designs, it is possible to optimize this device for maximum performance and utilize it for both personal and commercial applications.

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Environment-friendly Biodiesel Production from Waste Animal Fats

Islam Uddin Shipu*, Animesh Kumar Biswas, Salma A. Iqbal, Abu Yousuf, Md. Shahadat Hossain

Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology,
Sylhet-3114, Bangladesh

Received: 16 August 2021; Accepted: 19 October 2022; Published: 30 April 2023

Abstract: As fossil fuels are limited sources of energy, this increasing demand for energy has led to a search for alternative sources of energy that would be economically efficient and environmentally sound. The purpose of this work was to utilize available animal fat waste to produce biodiesel through transesterification. Extracted oil from beef tallow was trans esterified with methanol in presence of a KOH catalyst. The condition for transesterification was 5:1 methanol:oil molar ratio, 55-60°C temperature for are action time of 10 hours. The resulting products were confirmed by FTIR and evaluated by ASTM analyses. The resulting biodiesel exhibited moderate density (0.875g/cm³), average dynamic viscosity (4.98 Cp at 40°C), average kinematic viscosity (5.70 cSt at 40°C), high flash point (162°C), low cloud point (4°C), low pour point (-1°C), and high calorific value (11175.20 BTU/lb).

Keywords: alternative energy, biodiesel, transesterification, FTIR, fuel characteristics

1. Introduction

During the last century, the consumption of energy has increased due to the change in lifestyle and significant growth of the population. This increase in energy demand has been supplied using fossil resources, which caused the crisis of fossil fuel depletion, the increase in its price and serious environmental impacts such as global warming, acidification, deforestation, ozone depletion, Eutrophication and photochemical smog. As fossil fuels are limited sources of energy, the increasing demand for energy has led to a search for alternative sources that are economically efficient, socially equitable, and environmentally sound.

Two of the main contributors to this increase in energy demand are transportation and the basic industry sectors. The transport sector is a major consumer of petroleum fuels such as diesel, gasoline, liquefied petroleum gas(LPG) and compressed natural gas (CNG) [5]. Demand for transport fuels has risen significantly during the past few decades. The demand for transport fuel has been increasing and expectations are that this trend will remain unchanged for the coming decades. In fact, with a worldwide increasing number of vehicles and a rising demand for emerging economies, demand will probably rise even harder. Transport fuel demand is traditionally satisfied by fossil fuel. However, resources of these fuels are running out; prices of fossil fuels are expected to rise. In addition, combustion of fossil fuels has detrimental effects on the climate. The expected scarcity of petroleum supplies and the negative environmental consequences of fossil fuels have spurred the search for renewable transportation biofuels [8]. Biofuels appear to be a solution to substitute fossil fuels because sources will not run out, they are becoming cost competitive with fossil fuels, they are more environment-friendly and are available for distribution and use.

Conventional fuels, however, are predicted to become scarce) as 'petroleum reserves are limited [5]. As a result, these fuels are set to become increasingly costly in the coming decades. Renewable fuels, made from biomass, 'have enormous potential and can meet the present world energy demand[3]. Biomass can be used for energy in several ways; one of these is the conversion into liquid or gaseous fuels such as ethanol and bio-diesel for use in mobile source combustion[13].

The potential of biofuels appears to be enormous from an economic, political and environmental perspective. The advantages of biofuels are manifold. They appear to be more environment-friendly in comparison to fossil fuels considering the emission of greenhouse gasses when consumed. The energy content of biofuels differs from conventional fuels. Total energy output per liter of biofuel is determined by the feedstock used, region where the feedstock is grown, and production techniques applied. For example, biodiesel has an energy ratio compared to diesel of about 1.1 to 1, which means that its energy contents are 87% of those of diesel[17].

Biodiesel production is a very modern and technological area for researchers as an alternative fuel for diesel engines because of the increase in the petroleum price, its renewability and the environmental advantages. Biodiesel can be produced from renewable sources such as vegetable oil, animal fat and used cooking oil. Currently, the cost of biodiesel is high as compared to conventional diesel oil because most of the biodiesel is produced from pure vegetable oil. Extensive use of edible oils may cause other significant problems such as starvation in developing countries. However, the cost of biodiesel can be reduced by using low-cost feedstock such as waste animal fat. It is estimated that the cost of biodiesel is approximately 1.5 times higher than that of diesel fuel due to the use of food grade oil for biodiesel production. It is reported that the prices of biodiesel will be reduced approximately to half with the use of low cost feedstock[16]. In the last years, meat production has increased significantly. World meat production reached 237.7 million tons in 2010, from which 42.7%, 33.4%, 23.9% corresponds to respectively pork, poultry and beef (Fedderm et al., 2010). Consequently, a large volume of residues from animal processing-plants has been generated in countries with intensive livestock production. Within agro-industrial residues, lipid sources may be used as feedstock to biodiesel supply, helping to solve inappropriate environmental disposal, besides contributing to energy demand[6].

* Corresponding Author: Islam Uddin Shipu,
E-mail: islamshipu68@gmail.com

Biodiesel is a renewable and clean source of energy. Biodiesel production from animal fat through transesterification is non-polluting. No combustion takes place in the process, meaning there is zero emission of greenhouse gasses to the atmosphere. Therefore, using biodiesel from waste as a form of energy is a smart way to combat global warming. Biodiesel generation helps cut reliance on the use of fossil fuels. In addition, the raw materials (animal fats) used in the production of Biodiesel are renewable as animals will continue to grow.

The objective of the current study was to collect pure fat and residual fat from slaughterhouse for conversion to oil by heating process. Extracted oil was trans esterified with methanol to produce biodiesel. The biodiesel produced was analyzed for various parameters by applying ASTM standard methods. Properties of biodiesel were compared with international standards to measure its quality.

2. Materials and Methods

2.1 Collection of animal fats

Beef tallow was collected from a butcher shop in Sylhet and transferred in the laboratory for further processing.

2.2 Processing and analysis of fats

2.2.1 Washing and heating

The tallow collected was washed with water to remove dust and other external materials. Then it was heated at 100°C for 90 minutes on a hot plate to extract oil from pure and residual waste.

2.2.2 Filtration

The extracted oil was filtered to remove impurities such as residual meat pieces.

2.2.3 Transesterification process

Transesterification reaction was carried out using 5:1 molar ratio of methanol to oil. 200 ml of the oil extracted from beef tallow were mixed with 40 ml methanol and 2.8-gram KOH with continuous stirring for 10 minutes at 55-60°C. After the reaction was complete, the sample was kept in a separating funnel for 8-10 hours to separate biodiesel from residual glycerin. The resulting upper layer was distinguished as biodiesel, while the lower layer as glycerin.

2.2.4 Biodiesel production and analysis

The glycerol was removed from the bottom of the separatory funnel. The biodiesel produced was then washed with distilled water to remove excess methanol, KOH and unwanted soap. After washing, the biodiesel was dried overnight in an oven at 105°C. Then the biodiesel was ready for use.

2.2.5 Characterization of biodiesel

The properties of biodiesel such as kinematic viscosity, dynamic viscosity, flash point, density, pour point, cloud point and calorific value were measured to analyze the quality of the biodiesel produced by following ASTM D-445, D-445, D-93, D-1298, D-97, D-5773 and D-240 protocols, respectively.

3. Results and Discussion

3.1 Oil extraction from beef tallow

The beef tallow was taken in both pure and residual forms. The percentage extraction of oil was different for each sample. In case of residual tallow, one kilogram of residual beef tallow was converted into 54.17% oil. On the other hand, one kilogram of pure beef tallow was converted into 89.01% oil. The difference in the conversion rates may be owed to the presence of several impurities like free fatty acids, Na, K, Ca, Mg, P, unsaponifiable matter and humidity in residual tallow (Morales et al., 2011).

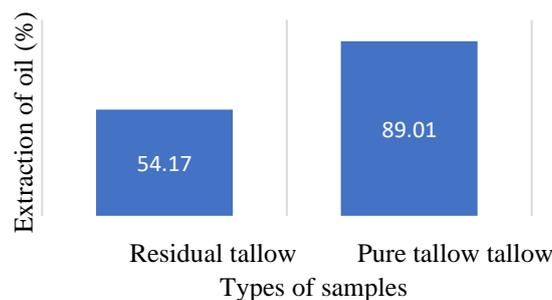


Figure 1: Percentage extraction of oil from pure and residual beef tallow.

3.2 Beef tallow analysis

The beef tallow was analyzed for the following properties. The results obtained are shown in Table 1.

3.2.1 Density

Density at 25°C of beef tallow was 0.921 g/cm³. The ASTM standard for the density of beef tallow at 25°C is 0.920 g/cm³[18]. Density of used vegetable oil (cooking oil) varies between 0.904 and 0.918 g/cm³[4]. Therefore, beef tallow can be also used as cooking oil.

3.2.2 Viscosity

The dynamic and kinematic viscosity of beef tallow at 40°C was 38.1cP and 43.85cSt, respectively. The ASTM standard for dynamic and kinematic viscosity of beef tallow at 40°C are 42.6cP and 46.37cSt, respectively[14]. Therefore, it can be said that the values of the viscosities determined were within the acceptable range.

3.2.3 Flash point

The flash point of beef tallow was determined at around 190°C. The ASTM standard flash point of beef tallow is 202°C (Lezsovits et al., 2012).

3.2.4 Water Content

The beef tallow used was completely water free. According to the study conducted by Lezsovits et al (2012) [12], the moisture content in animal beef tallow was found to be 0.00%.

Table 1: Properties of beef tallow.

Specifications	Beef Method	ASTM Standards	
		Results	Methods
Density at 25°C (g/cm ³)	0.921	0.920	ASTMD-12980
Dynamic Viscosity at 40°C (cP)	38.10	42.60	ASTMD-445
Kinematic Viscosity at 40 (cSt)	43.85	46.37	ASTMD-445
Flash Point (°C)	190.0	202.0	ASTMD-93
Water Content (%)	0.00	0.00	ASTMD-95

3.3 Biodiesel analysis

The biodiesel produced from beef tallow was analyzed for the following properties. The results obtained are shown in Table 2.

3.3.1 Density

The density of the biodiesel obtained was 0.875 g/cm³ at 25°C. The ASTM standard for density of biodiesel at 25°C is 0.86-0.90 g/cm³[2]. In this study, the density of the biodiesel produced is within this range. Therefore, it can be said that the value of the density determined was within the acceptable range.

3.3.2 Dynamic Viscosity

The dynamic viscosity of the biodiesel produced was found to be 4.98cP at 40°C. The ASTM standard for dynamic viscosity of biodiesel at 40°C is 4.698cP[14]. The dynamic viscosity of the biodiesel produced is approximately equal to the standard value and therefore can be said to be within acceptable range.

3.3.3 Kinematic Viscosity

The kinematic viscosity of the biodiesel at 40°C was found to be 5.70cSt; the ASTM standard value is 1.9-6.0cSt[10]. Kinematic viscosity is an important element in the performance of fuels used in engines as both low and high viscosities can have negative effects on engine performance. While low viscosities do not provide sufficient lubrication for the precision fit of fuel injection pumps, high viscosities leads to the formation of large droplets upon injection[10]. As the kinematic viscosity of the biodiesel produced is within the standard values, therefore it may be used as a fuel for engines.

3.3.4 Flash point

The flash point of the biodiesel was found to be approximately 162°C. The ASTM standard for flash point of biodiesel is greater than 130°C[11]. Fuels with higher flash points are less flammable or hazardous than fuels with lower flash points. Therefore, using the biodiesel produced as fuel would pose lower risk.

3.3.5 Cloud point

The cloud point of the biodiesel was recorded at 4°C. The ASTM standard for cloud point of biodiesel is 13°C[9].

3.3.6 Pour point

The pour point of biodiesel was found to be approximately -1°C . There is no standard value for pour point on the ASTM standards list of biodiesel. Heikal et al (2017)[7] determined the pour point of biodiesel produced from *Jatropha oil* at 3°C . Therefore, the pour points of two different oil-based biodiesels are comparable.

3.3.7 Calorific value

The calorific value for biodiesel was found to be 11175.20 Btu/lb. The ASTM standard for calorific value of biodiesel is 10907.4 Btu/lb[1]. The calorific value of the biodiesel produced is less than diesel (19706 Btu/lb)[10]. However, biodiesel is economically efficient and environmentally sound than diesel.

Table 2: Properties of biodiesel derived from beef tallow.

Specifications	Beef Method	ASTM Standards	
		Results	Methods
Density at 25°C (g/cm^3)	0.875	0.86-0.90	ASTMD-1298
Dynamic Viscosity at 40°C (cP)	4.98	4.698	ASTMD-445
Kinematic Viscosity at 40°C (cSt)	5.70	1.9-6.0	ASTMD-445
Flash Point ($^{\circ}\text{C}$)	162	>130	ASTMD-93
Cloud Point ($^{\circ}\text{C}$)	4	13	ASTMD-5773
Pour Point ($^{\circ}\text{C}$)	-1	-----	ASTMD-97
Calorific Value (Btu/lb)	11175.20	10907.4	ASTMD-240

3.4 Effect of temperature on dynamic viscosity of biodiesel

The effect of temperature on the dynamic viscosity properties of the biodiesel is shown below (Figure 2). The figure shows that with increasing temperature, the dynamic viscosity of the biodiesel decreases.

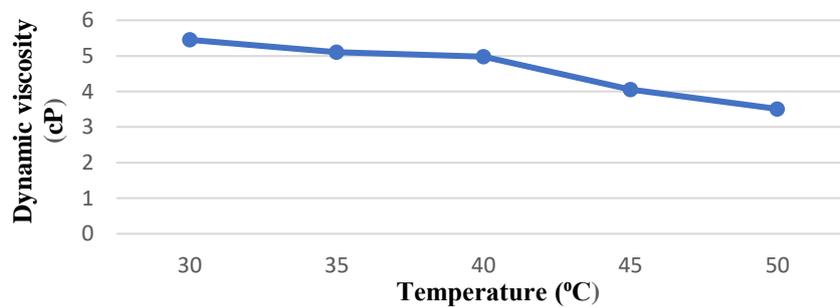


Figure 2: Behavior of dynamic viscosity of biodiesel with the changes of temperature.

3.5 Effect of temperature on kinematic viscosity of biodiesel

The effect of temperature on the kinematic viscosity properties of the biodiesel is shown below (Figure 3). According to the figure, with increasing temperature, the kinematic viscosity of the biodiesel decreases.

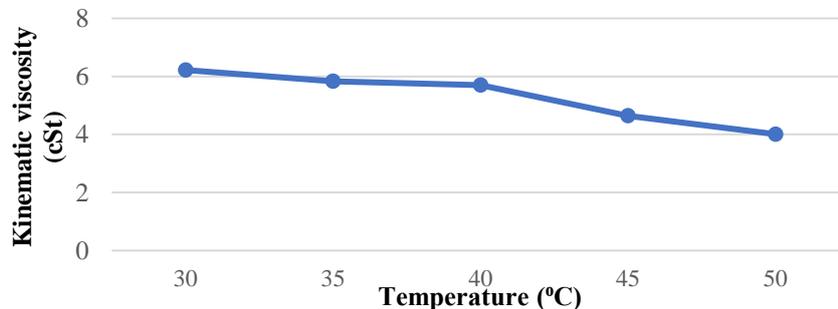


Figure 3: Behavior of kinematic viscosity of biodiesel with the changes of temperature.

3.6 Fourier-transform infrared spectroscopy (FTIR) analysis for biodiesel

To investigate the chemical composites of the biodiesel (beef tallow methyl ester) produced, fourier transform infrared spectroscopy (FTIR) test was performed, the result of which is shown below (Figure 4). The FTIR spectrum of biodiesel clearly shows the absorption band in the region of $2855\text{--}3000$ cm^{-1} and $1350\text{--}1480$ cm^{-1} due to C–H stretching vibration. This indicates identical functional group of alkane in their molecular structure[7] as the absorption band for petroleum diesel, which is in the region of $2855\text{--}3000$ cm^{-1} and $1350\text{--}1480$ cm^{-1} , indicating the presence of C–H functional group. Besides, the FTIR spectrum of biodiesel shows new absorption bands in the region of $1670\text{--}1820$ cm^{-1} , which indicates

the presence of the C=O functional group. The other sharp peak at 1170.79 cm⁻¹ indicates the presence of oxygen in the biodiesel produced. These peaks indicate that the biodiesel transesterification reaction was close to completion.

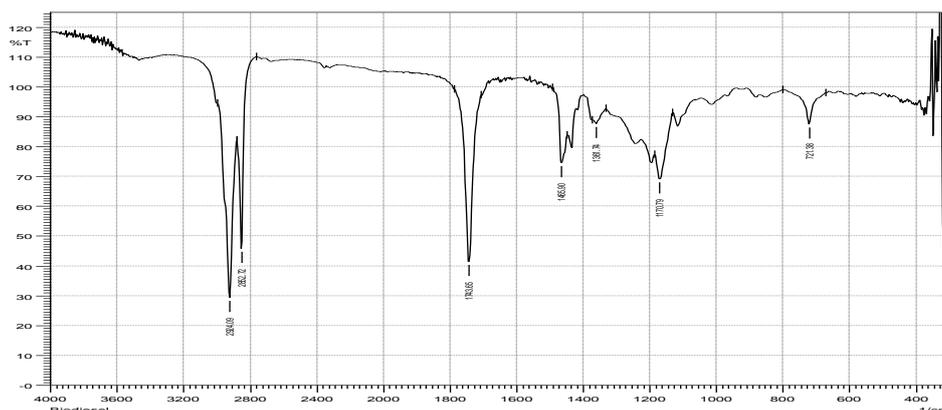


Figure 4: IR spectra of biodiesel (beef tallow methyl ester).

4. Conclusion

In terms of availability and low cost, compared to virgin vegetable oils, animal fat wastes (AFW) have been proven to be potential feedstocks for good quality biodiesel production. The use of AFWs as biodiesel feed stock reduces production costs and environmental damage. Combustion of animal fat-based biodiesel has been shown to produce lesser NO_x emission than vegetable oil-based biodiesel. Over the last years, meat production has increased significantly attaining 237.7 million tons in 2010, of which 42.7%, 33.4%, 23.9% correspond to pork, poultry and beef, respectively[6]. As a result, large volumes of residues from animal processing-plants is generated in countries with intensive livestock production. Within the agro-industrial residues, lipid sources may be used to solve inappropriate environmental disposal of the animal wastes, besides contributing to energy supply. Biodiesel has a higher flash point than fossil diesel and is safer in the event of crash. Besides, other biodiesel properties such as density, viscosity, cloud point, pour point, calorific value are comparable to commercial industrial oil.

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An optimization study of methylene blue dye treatment in synthetic textile wastewater by Fenton oxidation process

Md. Burhan Kabir Suhan, Niaz Mahmud, Muhammad Hasanur Arefin Shahria,
Md. Shahinoor Islam*

Department of Chemical Engineering, Bangladesh University of Engineering and Technology,
Dhaka -1000, Bangladesh.

Received: 13 September 2021; Accepted: 2 November 2022; Published: 30 April 2023

Abstract: Methylene blue (MB), an azo dye, is water-soluble and bio persistent because of its complex aromatic ring structure. Along with its carcinogenic, toxicogenic, and mutagenic nature, the MB dye can decrease the photosynthetic activity of aquatic plants. Therefore, the objective of the current study was to treat and optimize the treatment of MB dye in synthetic wastewater by the Fenton oxidation process and to determine the degradation's kinetics. To analyze the performance of the treatment, color, TDS, TSS, TS, turbidity, BOD and COD removals were assessed after the treatment of synthetic textile wastewater. The optimum dosing of $\text{FeSO}_4/\text{H}_2\text{O}_2$ was found 200 ppm/2.4 mL for the treatment and the corresponding reaction time for this optimum dose was 180 min. A noticeable reduction of color (>85%), COD (>85%) and turbidity (>70%) were observed from the study. The kinetic study demonstrated that COD, TDS and BOD degradation follows the second-order model satisfactorily. The rate constants were found 0.09×10^{-5} - $6 \times 10^{-5} \text{ Lmg}^{-1}\text{min}^{-1}$ and half-lives were found at 3.2-30 min in second order model. Based on the performance of Fenton process, it can be concluded that Fenton oxidation process can be a better option for the treatment of textile wastewater.

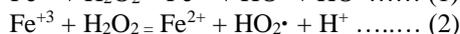
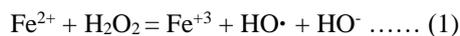
Keywords: Fenton, methylene blue, ferrous sulfate, hydrogen peroxide, textile wastewater, kinetics

1. Introduction

In developing countries like Bangladesh, textile industries are severely polluting surface water by discharging tons of wastewater daily. This wastewater contains dyes, surfactants, and other organic and inorganic pollutants. These dyes are stable to light, heat, and conventional oxidizing agents and have persistent behaviour to aerobic biodegradation [1,2]. Therefore, it cannot be removed after applying conventional physicochemical and biological treatments. In addition, the Department of Environment (DoE) will soon implement a zero-discharge policy, which is a significant concern for the sustainable development of textile industries in Bangladesh. In this context, an effective treatment scheme for this effluent is urgently required before it is released into the surface water.

The conventional treatment methods applied coagulation-flocculation [3] and biological [4], treatments followed by sand filtration and adsorption [5,6] for the treatment of textile wastewater. However, it has been reported that, the conventional biological wastewater treatment process can hardly degrade azo dyes [7]. Physicochemical method has some constraints to the generation of large volumes of sludge, cost of chemical consumption and energy cost, etc. [8,9]. It is also inefficient due to bio-persistent and toxic nature of the dyes [10]. The adsorption process has a limitation of higher cost and adsorbent being contaminated in the recovery process [5,7]. Recently, it has been shown that advanced oxidation processes (AOPs) are promising in degrading dye containing wastewater. Among these methods, electrochemical [7], ozonation [11], persulfate degradation [12], Fenton [13] and nano-photocatalyst treatment have been applied efficiently [14-16]. These processes are very promising in destroying organic pollutants like textile dyes, naphthenic acids, cosmetics, and pharmaceutically active ingredients [10,15,17]. AOPs generate strong oxidizing hydroxyl radicals ($\cdot\text{OH}$, $E^0 = 2.8\text{V}$ versus NHE) capable of mineralizing organic pollutants to CO_2 and water [15].

Fenton oxidation process is one of the convenient AOPs treatments which can be used to degrade textile dyes, either independently or in combination with other conventional treatments. In this process, Fenton's reagent (a mixture of H_2O_2 and Fe^{2+}) is used where Fe^{2+} act as a catalyst, breaks down H_2O_2 to generate $\cdot\text{OH}$ [18]. It is an effective process to degrade toxic and/or non-biodegradable compounds i.e., nitro-aromatics, aliphatic compounds, azo-dyes, phenols, etc., with the achievement of high reactions yields [19]. The primary mechanism of the Fenton process is explained in Eqn (1) and Eqn (2). Eqn (1) represents the generation of $\cdot\text{OH}$, and Eqn (2) represents the catalytic formation of the Fe^{2+} ion.



The effectiveness of the Fenton process depends mainly on the generation of $\cdot\text{OH}$. Optimum dosage of the operational molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ is essential to achieve the best output from Fenton process [20]. A higher dosage of Fenton reagent results in lower COD reduction and color removal efficiency due to the scavenging effect of $\cdot\text{OH}$ with the reaction of excess Fe^{2+} and H_2O_2 [21]. In addition, excess Fe^{2+} can contribute to total dissolved solids (TDS) content of the effluent stream, which is an undesirable phenomenon [22].

H_2O_2 concentration in treated wastewater is an important factor and contributes significantly to the removal of organics. Generally, increasing the H_2O_2 concentration leads to increasing the degradation of the pollutants because more $\cdot\text{OH}$ are produced, which degrade the color, COD and BOD [23].

pH of the treated wastewater is also a vital parameter of the degradation process. Initial pH can slower or faster the degradation rate of COD and phenol compounds [24]. At higher pH (generally above 4), oxidation potential of $\cdot\text{OH}$

* Corresponding Author: Md. Shahinoor Islam,

E-mail: shahinoorislam@che.buet.ac.bd

decreases rapidly and the activity of Fenton reagent decreases for the existence of inactive iron oxo-hydroxides and the formation of ferric hydroxide precipitate. In addition, iron species can inhibit the reaction between Fe^{2+} and H_2O_2 [25]. On the other hand, at low pH values (generally below 2.5), iron complex species $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ forms, which reacts more slowly with H_2O_2 than other species [26].

Methylene blue (MB) is a cationic dye because it forms a coloured cationic salt when dissolved in wastewater. Cationic dyes are significantly more harmful than anionic dyes. Since MB dye is extensively used in textile dyeing, paper, pharmaceutical, cosmetics, plastics, rubber, leather and food industries, an efficient treatment method is urgently required for degrading this dye [27,28].

In this study, a model was developed to investigate the optimum molar ratio, optimum dosage, and optimum reaction time required for Fenton based AOP's treatment of synthetic textile wastewater containing MB dye. The experiment explored both the advantages and disadvantages of Fenton based AOP's. A rate-based model has also been derived at the end of kinetic analysis, indicating the reaction order, rate constant and half-life of the reaction.

2. Materials and Methods

2.1. Materials

The materials used in this study are:

Analytical grade ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), H_2O_2 solution (30% w/w; density 1.07 g/cm^3), sulfuric acid (98% purity, density 1.84 g/cm^3), sodium hydroxide pellet, sodium carbonate and acetic acid (99%). All the chemicals mentioned above were purchased from Merck Company, Germany. Sodium chloride (99% w/w), detergents (SLS) and food-grade starch were purchased from a local laboratory supply chemical store. Textile grade MB dye (Chemical formula $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) was collected from a local company Jamuna Denims Limited.

2.2. Synthetic textile wastewater preparation

Synthetic textile wastewater was prepared according to the constituents shown in table 1 [29]. The room and wastewater temperatures were nearly $24 \text{ }^\circ\text{C}$ and $23 \text{ }^\circ\text{C}$, respectively.

Table 1. Chemical constituents used for the preparation of synthetic textile wastewater

Materials	Concentration	Function
Starch	1000 mg/L	Sizing agent
Acetic acid	0.20 mL /L	Sizing agent
Dye (Methylene Blue)	251 mg/L	Coloring agent
Caustic Soda	512.5 mg/L	Hydrolysis
Sodium Carbonate	501.5 mg/L	Fixing agent
Sulfuric Acid	0.301 mL/L	pH control
Detergents	128.5 mg/L	Scouring agent
Sodium Chloride	3076.5 mg/L	Fixing agent

2.3. Methods and analysis

The synthetic textile wastewater treatment was performed in a batch reactor. The schematic diagram of the experimental set-up used for this process is shown in Figure 1. The reactor was a 500 mL beaker made of quartz glass. Initial physicochemical parameters of the synthetic textile wastewater and experimental procedure of the solution preparation have been shown in Table 2 and Figure 2, respectively.

Color analysis and COD were determined via the spectrophotometer (HACH-DR/4000US) using a dichromate solution as the oxidant in a strongly acidic medium [30]. TDS was measured by Hanna-edge HI2030-01. Before calculating the BOD_5 , the wastewater was adjusted to neutral pH at seven by adding Na_2CO_3 [31]. Other instruments used in experiments are weight machine (Vibra and XB-220A Precisa) and desiccator for TS analysis (GCA Precision Scientific Model 68351, heated vacuum desiccator).

Table 2. Physicochemical parameters of synthetic textile wastewater.

Parameter	Unit	Quantity
Color	Pt-Co	2100
Turbidity	FAU	6200
TDS	gm/L	3.70
TS	gm/L	5.30
TSS	gm/L	1.89
BOD	mg/L	180
COD	mg/L	524
pH	-	10.3

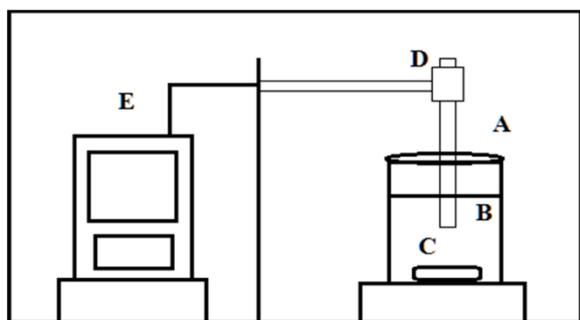


Figure 1. Set up for the experiment. A- Reaction beaker, B- Wastewater solution, C- Magnetic stirrer, D- Electrode measuring pH, E- pH meter.

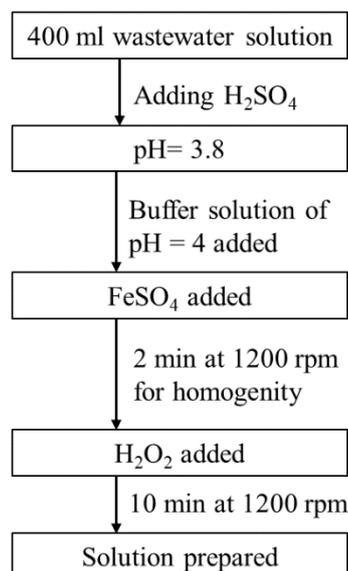


Figure 2. Steps of solution preparation for Fenton treatment.

2.4. Kinetic study

MB dye removal kinetics has been performed for zero-order, first-order and second-order model with respect to degradation of TDS, COD and BOD with time. The integrated form of above kinetic models are presented by Eqns. 3-8 [7]

Zero order kinetics:

$$C - C_0 = k_0 t \quad (3)$$

$$t_{1/2} = \frac{C_0}{2k_0} \quad (4)$$

First order kinetics:

$$\ln\left(\frac{C_0}{C}\right) = k_1 t \quad (5)$$

$$t_{1/2} = \frac{\ln 2}{k_1} \quad (6)$$

Second order kinetics:

$$\frac{1}{C} - \frac{1}{C_0} = k_2 t \quad (7)$$

$$t_{1/2} = \frac{1}{k_2 C_0} \quad (8)$$

Where k_0 ($\text{mg.L}^{-1}.\text{min}^{-1}$), k_1 (min^{-1}) and k_2 ($\text{L.mg}^{-1}.\text{min}^{-1}$), represent the apparent kinetic rate constants of zero, first and second-order reaction kinetics, respectively. C_0 (mg.L^{-1}) and C (mg.L^{-1}) are the initial dye concentration and dye concentration at time t (min), respectively.

3. Results and Discussions

3.1. Optimum molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$

The optimum molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ was evaluated by changing moles of H_2O_2 where moles of Fe^{2+} remained constant. A total of 8 experiments have been conducted by varying the molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ from 1/1.5 to 1/21.4 and the optimum molar ratio has been determined from their degradation capability of color, COD and BOD. Figure 3 shows that when the molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ approached 1/14.5 the degradation capability of color, BOD and COD reached equilibrium. After that point, there was no significant changes in degradation with addition of H_2O_2 . Thus, optimum molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ was 1/14.5 [32]. During each experiment concentration of FeSO_4 remained constant at 250 ppm. Initially, the pH of the solution was maintained near 3.80. But the addition of 250 ppm FeSO_4 reduces the pH to 3.05 due to its acidic behaviour in solution. On the other hand, H_2O_2 addition has no impact on pH rise or drop.

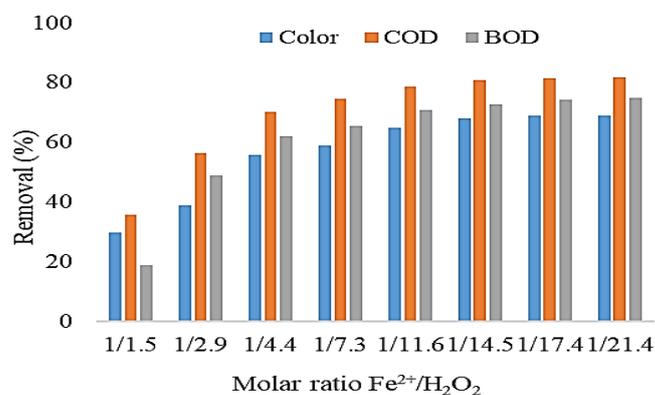


Figure 3. Removal percentage of color, BOD and COD with respect to molar ratio of Fe²⁺/H₂O₂ after 20 hours keeping fixed [Fe²⁺] = 250 ppm (1.65 m.moles).

3.2. Optimum dosing point determination while molar ratio of Fe²⁺/H₂O₂ is 1/1.14

In order to find out the optimum dosing point a total of 10 experiments have been conducted by changing the dose of Fe²⁺ and H₂O₂ while keeping the optimum molar ratio of Fe²⁺/H₂O₂ (1/14.5) constant. Fe²⁺ concentration varied from 10-1250 mg.L⁻¹ with corresponding H₂O₂ dose. Table 3 represents the removal percentage of TDS, TS, color, turbidity and COD with the change of Fe²⁺ and H₂O₂ concentration. pH of the solution decreased continuously with the addition of FeSO₄ (from 3.8 to 2.42 when Fe²⁺ added from 10 mg.L⁻¹ to 1250 mg.L⁻¹) because FeSO₄ dissolution in water produces more H⁺ hence the wastewater became more acidic. Except TS, in all cases the highest removal was obtained on 200 ppm Fe²⁺ concentration and 2.4 ml (30% w/v) H₂O₂ dose.

The initial TDS, TS, color, turbidity and COD concentrations are shown in table 2. As the rise of Fe²⁺ concentration from 10 ppm, removal efficiencies of all the parameters increased continuously up to 200 ppm. After that, the removal efficiencies decreased significantly with the addition of Fe²⁺. The highest removal of TDS, TS, color, turbidity, COD were found 43% (at 200 ppm Fe²⁺), 42% (at 150 ppm Fe²⁺), 88% (at 200 ppm Fe²⁺), 72% (at 200 ppm Fe²⁺) and 87% (at 200 ppm Fe²⁺), respectively. Therefore, the optimum dose of the Fe²⁺ was 200 ppm. After the optimum dosing point TDS removal percentage was decreased because of excessive iron accumulation and drop of pH of the treating solution. The drop of color removal percentage after optimum dose might be due to the excessive amount of FeSO₄ that may impact the color measurement. Excessive iron accumulation, low pH and less reaction propagation or smaller organic formation in the unfavorable environment after a particular point might decrease the turbidity removal percentage after 200 ppm as shown in table 3. The reduction percentage of TS (total solid) was maximum at 150 ppm of MB dye concentration. The presence of unreacted FeSO₄ might be the reason of decreasing of removal percentage of TS at higher Fe²⁺ concentration. Again, excessive Fe²⁺ may lead to pH (optimum pH 4.0-3.0) lower than the optimum level, resulting in less reaction between organic compounds and reactive hydroxyl radicals. That's why, after a specific dose catalytic oxidation process was not effective.

Table 3. Removal percentage of TDS, TS, color, turbidity, COD for a fixed molar ratio of Fe²⁺: H₂O₂=1:14.5.

FeSO ₄ (ppm)	Removal percentage (%)				
	TDS	TS	Color	Turbidity	COD
10	7	12	19	39	28
50	6	21	43	56	45
100	16	33	62	60	53
150	30	42	85	68	81
200	43	41	88	72	87
250	28	37	68	70	83
350	16	35	38	69	86
500	3	19	31	63	85
750	2	13	29	60	79
1250	2	13	23	56	72

3.3. Effect of reaction time on optimum dosing

For 200 ppm FeSO₄ and 2.4 mL H₂O₂ dose, the degradations of specific parameters (color, TDS, COD and BOD) were observed for 225 min, and the results have been illustrated in figure 4. From figure 4, it can be seen that color change was initially fast due to availability of the reactant. After 180 minutes, the color of the wastewater was nearly 250 Pt-Co and no effective removal was observed after that time (180 min). Similar results can be seen for other parameters except TDS. At 180 min of reaction time, COD value reached nearly 70 mg/L and became equilibrium in that value. Similar

results were achieved in BOD degradation. However, TDS degradation didn't reach the equilibrium value within the reaction time of 180 min. The rate of TDS degradation was slow (figure 4), which might lead it to reach the equilibrium time slightly greater (225 min) than optimum color, COD and BOD degradation time. It is known that Fenton type oxidation continues for a longer period as long as Fe^{2+} and H_2O_2 available within the reactor. Still, the reaction rate becomes very slow after a certain period. In this study, the aforementioned period was found 180 min for color, COD and BOD but 225 min for TDS removal.

3.4 Kinetics analysis

Kinetic study has been performed following the zero-order, first-order and second-order models for TDS, COD and BOD degradation. Kinetic plots of them have been illustrated in figure 5 and the calculated parameters of the model have been shown in table 4. Comparing the regression coefficient (R^2) shown in table 4 and figure 5, it can be seen that TDS, COD and BOD degradation follows second-order kinetic model. R^2 values were found at 0.99, 0.96 and 0.93 for TDS, COD, and BOD in the second-order model [33]. The rate constants (k_2) were found $0.09 \times 10^{-5} \text{ Lmg}^{-1}\text{min}^{-1}$, $6 \times 10^{-5} \text{ Lmg}^{-1}\text{min}^{-1}$ and $6 \times 10^{-5} \text{ Lmg}^{-1}\text{min}^{-1}$ while half-lives were found 30 min, 3.2 min and 9.3 min for TDS, COD, BOD, respectively in the second-order model. Apart from the second order, the first-order kinetic model also fitted well (better than second order in COD degradation kinetics) where R^2 values were found 0.99, 0.94 and 0.79 for TDS, COD and BOD, respectively. Zero-order fitted well on TDS degradation only but very poor in other two. Half-lives of them have been calculated and the calculated data were placed in Table 4.

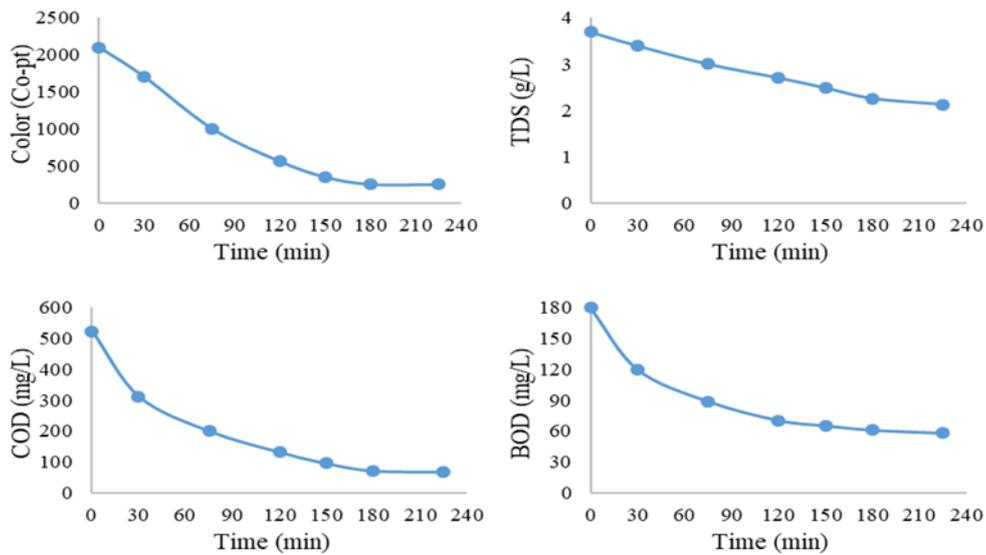


Figure 4. Degradation of Color, TDS, COD and BOD when Fe^{2+}/H_2O_2 molar ratio = 1/1.14 and dosing 200 ppm/2.4ml

Table 4. Kinetic parameters for zero-order, first-order and second-order model

Analytical methods		TDS	COD	BOD	
Kinetic parameters	Zero-order	$k_0(\text{mg.L}^{-1}.\text{min}^{-1})$	7.67	2.58	0.69
		R^2	0.98	0.65	0.57
		$t_{1/2}$ (min)	241	101	130
	First-order	$k_1 \times 10^{-3}(\text{min}^{-1})$	2.60	10.50	6.20
		R^2	0.99	0.94	0.79
		$t_{1/2}$ (min)	267	66	112
	Second-order	$k_2 \times 10^{-5}(\text{L.mg}^{-1}.\text{min}^{-1})$	0.09	6.0	6.0
		R^2	0.99	0.96	0.93
		$t_{1/2}$ (min)	30.0	3.2	9.3

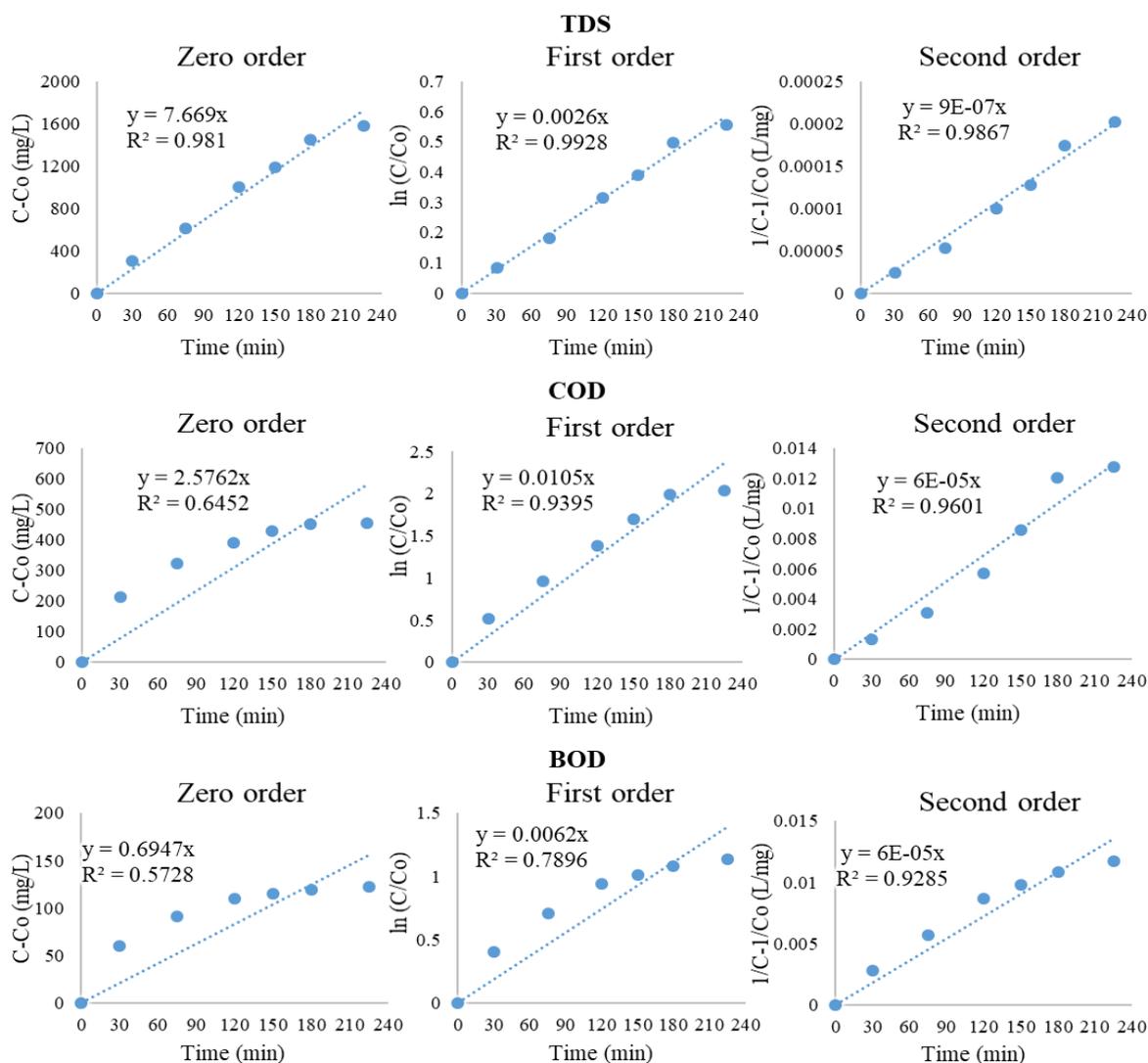


Figure 5. Kinetic plots of zero-order, first-order and second-order model for TDS, COD and BOD degradation

4. Conclusion

The optimum molar ratio of Fe^{2+}/H_2O_2 and optimum time were found to be 1/14.5 (at optimum Fe^{2+} dose of 200 ppm) and 180 min, respectively, for the degradation of synthetic textile wastewater containing MB dye. The degradation reaction follows the second-order kinetic model. The process is highly efficient for color, COD and BOD removal, however, the reduction efficiency of TDS, TSS, TS was not satisfactory. The excessive iron accumulation and formation of small molecule from breaking large organic compounds can probably be a barrier in TDS, TSS, TS removal efficiency. Our results therefore indicate that the Fenton oxidation process can be successfully utilized to remove color and COD from MB dye containing textile wastewater.

Acknowledgment

The authors acknowledge Bangladesh University of Engineering and Technology (BUET) for contributing financial support for the project and Department of Chemical Engineering, BUET for providing laboratory facilities.

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Journal of Chemical Engineering

Vol. ChE 31, No. 1, January 2023



The Institute of Engineers, Bangladesh (IEB)
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