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REVIEW ON PRODUCTION OF BENZENE FROM PETROLEUM ASSOCIATED GAS BY DEHYDRO-AROMATIZATION, PARTIAL OXIDATION OF METHANE AND METHANOL-TO-AROMATICS PROCESSES

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Abstract

Benzene is the most basic aromatic compound, which possesses diverse applications in the chemical industry. Benzene is mainly used as an intermediate chemical for styrene in the manufacturing of plastic materials. The benzene derivatives such as styrene, cumene, cyclohexane and nitrobenzene are the four most significant products, which are highly dependent on the benzene demand. However, there is a huge gap between the supply and demand of benzene, and fluctuation of the market price of benzene is also noticeable in recent years. Primarily, benzene is produced as a by-product especially from steam crackers, production of p-xylene and also in oil refineries. This caused the demand of benzene to follow strictly on gasoline, ethylene and also p-xylene in particular. Hence, in this review, three important benzene process pathways are studied and compared based on its economic, safety and environmental aspects in order to allow researchers to understand and able to compare different route of benzene production in terms of sustainability aspects for an on-purpose build of a benzene production plant, which is more economically viable. Three identified process are benzene from ethane (ETB), methane dehydroaromatization: Non-oxidative process (NO-MDA) and natural gas via Methanol synthesis (MTB). NO-MDA process was found to be the most sustainable process among the above. The processes are based on the decision matrix method.

Keywords: Benzene, Benzene from ethane, Methane dehydroaromatization, Natural gas via methanol synthesis, Non-oxidative process.

1. Introduction

Associated gas or associated petroleum gas is a form of natural gas that is present in a hydrocarbon reservoir along with crude oil. The associated gas consists of 72.2% of methane, 8.90% of ethane, 5.20% of propane, 2.80% of butane, 0.60% of pentane, 0.50% of hexane, 9.50% of carbon dioxide, 0.20% of water and 0.10% of nitrogen and the associated petroleum gas that was produced yearly to our plant is 45 MMscfd [1].

Based on studies by Petropeida [2], in a reservoir, associated gas is either present freely on top of crude oil due to its lighter weight or dissolves in the crude oil at very high pressure, however, bubbles out of the oil when the pressure is reduced and then the oil is brought up to the surface. Emam [3] commented that this crude oil by-product was usually flared and vented into the atmosphere, however, it is now recognized as a major environmental problem, causing about 400 MTA CO_2 greenhouse gas to be emitted to the environment, which leads to air pollution and global warming. Furthermore, unprocessed natural gas contains a mixture of hydrocarbons and other substances, which can form a variety of chemical compounds during combustion such as carbon monoxide and nitrogen dioxide gas that can cause severe air pollution and affects human health [1].

According to the latest estimates from the satellite data, 3.5% of the world's natural gas supply was wastefully flared, which is about 147 bcm burned in 2015 from 143 bcm in 2012, and Russia is the world's top gas flaring country, flaring about 21 bcm annually [4].

Flaring of associated gas does not only cause environmental degradation and human's health complications, however, it also creates a huge economic loss to the country. Hence, there is a need of making use of associated gas in a useful way for, e.g., by changing into a chemical product.

In the industrial sector, gases are used to produce commercialized petrochemical products. One of the most common petrochemicals is known as aromatics such as benzene. Benzene has huge commercial value in the market as it acts as a feedstock for a wide range of chemical derivatives. Nearly 55% of benzene produced has been converted to ethylbenzene, which acts as an intermediate product that is mainly used in the manufacturing process of styrene, a chemical that used to produce synthetic rubbers or plastic materials [4].

The market demand for benzene, increased to 43.7 million metric tons in 2013, an increase of 2.8% above benzene demand from 2012 [5]. This seemed to be a great opportunity for more supply on board as the demand is high in order to fill in the demand gap of benzene.

Benzene is widely used as a solvent in paints or chemical intermediate for the production of many chemical products in the manufacture of plastics, drugs, dyes, detergent and insecticides [6]. More than half of the benzene is used in the production of ethylbenzene, which 99% of it is then converted to styrene [7]. Styrene is essential as a feedstock of a common plastic material, called polystyrene for packaging materials, acrylonitrile-butadiene-styrene for automatic components and Styrene-Butadiene (SB) latexes for paper coating and more [8]. On the other hand, ethylbenzene is also used to make chemicals required in fuel and acts as a solvent in inks, varnishes and adhesives industry [8].

The global benzene consumption is expected to increase at an average rate of 2-3% annually. China is one of the biggest and important consumers of benzene, only then followed by the United States and Western Europe [9].

The global demand for benzene has been increasing from 27.3 million tonnes in 2000 to 29.2 million tonnes in 2010. It is forecasted that the demand will increase in 2020 to reach about 43 million tonnes and the benzene market is expected to grow at a CAGR of 3.8% [10].

The shortfall of benzene supply due to the reduction of by-product, flat gasoline demand, higher usage of ethanol and limitations on regulations have increased on-purpose build of benzene and creating interest in finding more economical feedstocks to produce benzene such as shale gas and natural gas [11]. Hence, this creates a great opportunity for a more on-purpose build of benzene through more sustainable and profitable technology. This review is needed to allow researchers to understand and able to compare different route in terms of sustainability aspects (economic, environmental and social). Table 1 shows the summary of the benzene market.

Table 1. Summary of benzene market [10].

Global outlook	Asia outlook
• The global consumption of benzene is increasing at an average rate of 2-3% annually.	• China is the biggest consumer and producer of benzene in recent years.
• It is expected that the demand for benzene will reach up to 43 million tonnes in 2020 growing at CAGR of 3.8%.	• Even though China has produced benzene on its own, due to the high demand and consumption about 11 MT, China still imported 9.11 MT of benzene from Japan, Thailand and Korea.
• The supply-demand gap of benzene is expected to experience a shortage of 5.4 MTA in 2025.	• China has become the key driver to strike the production of benzene in Asia and more Asian countries such as Thailand, Korea, Vietnam and India have started to manufacture benzene due to the tight supply and high demand.
• The price of benzene went up about 4% from August 2016 to August 2017 to United State Dollar (USD) 755.35/mt. The United States is currently facing a shortage of benzene supply and has to import about 20% of benzene.	

2. Discussion

2.1. Process selection and analysis

The current production route for benzene is through the typical naphtha cracking process and also as a by-product produced from p-xylene production. There is no on-purpose build of benzene in Malaysia yet. According to S&P Global Platts [7], the major suppliers of the benzene would be Lotte Chemical Titan Holding Bhd. (LCT), John Chemicals Sdn. Bhd., Gremont Agrochem (M) Sdn. Bhd. and Aromatics Malaysia Sdn. Bhd.

The existing gap of production and consumption of benzene in the targeted market (i.e., Global, Asia and Malaysia) can be pulled closer by building a new benzene production plant. However, the process pathways must be carefully selected as it would affect the profitability of the plant as well as the production throughout the entire 20 years of plant life cycle.

The three processes focus mainly on the production of benzene from associated gas or shale gas, which are yet to be implemented in an actual chemical plant:

- Production of Benzene from Ethane (ETB).
- Methane Dehydroaromatization: Non-Oxidative process (NO-MDA).
- Production of benzene from Natural Gas via Methanol Synthesis (MTB).

2.2. Production description of benzene from ethane (ETB)

Ethane from natural gas is usually rejected through pipelines due to its low market value [12], which can lead to a huge economic loss as ethane can be used to produce BTX product that has a very high market price and demand. According to Bamji [4], patent US8772563, a Pt-zeolite catalyst is able to convert ethane into valuable aromatics products such as benzene, toluene and p-xylene (BTX). Pt-zeolite catalyst could improve the conversion rate and selectivity of methane to desired products. Hence, more valuable aromatics compounds can be produced and thus using the Pt-zeolite catalyst is considered a more economically viable decision [13].

The process of ethane to BTX involves 3 main sections, which are: [14]. Section 1: Feed processing, reaction and initial separation of hydrogen. Section 2: Light separation section. Section 3: Separation and recovery of BTX and Heavy Aromatics Products

2.2.1. Feed processing, reaction and initial separation process

Section 1 involves the feed processing where the pressure of the raw feed (ethane) is lowered, said to be 320 psia in order to allow the mixing process with the recycle stream to occur under the operating pressure [15]. The recycle stream consists of hydrogen and a small amount of methane, which could help to reduce the coking of the catalyst within the reactor and maintain the conversion rate. Next, the catalytic reaction happened in the reactor with an operating temperature of 1150-1170 °C and pressure of 20 to 200 psia [15]. The chosen pressure would affect the size of the reactor and indirectly control the catalyst-based capital costs of the reactor. The main reactions are listed in Table 2 [14]. In the reaction, dehydrogenation process of ethane and propane occurs to form alkenes and alkanes that will be used to further cyclize to form naphthalene and aromatics product (BTX). In addition, the dehydrogenation reactions are an endothermic reaction as hydrogen is produced throughout the reaction [15].

The hydrogen produced from the reaction can be purified from the mixed stream of the process and can be sold as another product, after the separation process to separate the hydrogen from the vapour stream by using the membrane technology.

Table 2. Main reactions in ethane to benzene process [15].

Reactions
$3C_2H_6 \rightarrow C_6H_6 + 6H_2$
$2C_3H_8 \rightarrow C_6H_6 + 5H_2$

2.2.2. Light separation process

The light separation process begins once the reactor effluent has been cooled down. The product stream is separated to form a light hydrocarbon rich stream and heavy hydrocarbon-rich stream. Light hydrocarbon stream will route to the light separation section while heavy hydrocarbon will be routed to Section 3, the product separation section. In the light separation process, the distillation column is first used to separate the hydrogen and methane from the product stream. Then, the hydrogen and methane exit as top product while the remaining hydrocarbons product stream exit as the bottom product of the distillation column at 276 psia and 19 °F. The top product stream is feed into pressure swing adsorption unit to purify the hydrogen and then the splitter is used to separate the hydrogen stream into sale stream and recycle stream. According to Chen et al. [14], 15 mol% of hydrogen is recycled back to the reactor to prevent the coking of the catalyst that will reduce the efficiency of the catalyst.

The remaining hydrocarbons product stream exit as the bottom product of the distillation column at 276 psia and 19°F. This product stream will feed into another distillation column where all the light hydrocarbons like ethane and propane will be recycled back to the reactor in order to achieve a higher conversion rate. While the bottom product, which consists mostly of C_4 and C_5 hydrocarbons will be sent to Section 3 and mixed with the heavy hydrocarbon product from the reactor effluent for the product separation process.

2.2.3. Separation and recovery of benzene and heavy aromatics products

Section 3 separate the by-product such as 1,3,5- trimethylbenzene and BTX using distillation column. the 1, 3, 5- trimethylbenzene will be channelled to storage tank without further purification and the BTX will be further separated from the BTX mixture at a distillation column that runs at pressure 50 psia and temperature of 285 °F [14]. The separation process is able to produce 99.6 wt% of pure benzene as a distillate product of the distillation column. The process flow diagram is illustrated in Fig. 1.

This process utilizes cheaper feedstock in the associated gas, which is the ethane gas to convert to high market value product, benzene. However, up to this stage, there is no current chemical plant, which utilizes rejected ethane gas from the associated gas to produce benzene. Hence, this process is economically viable by turning rejected gas into a useful product and with high novelty.

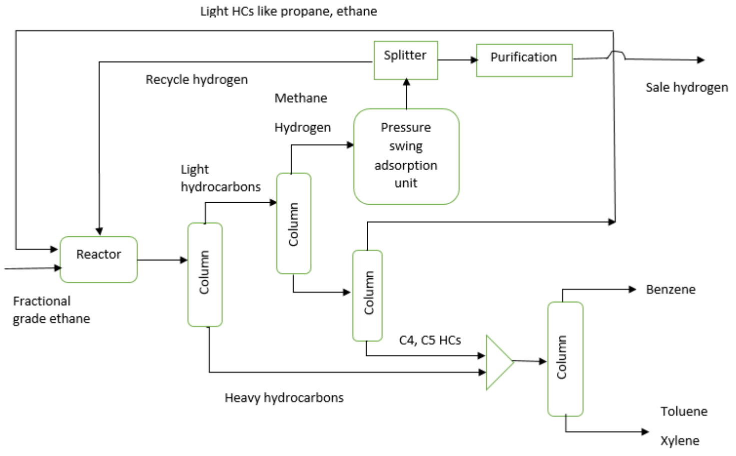

Fig. 1. Illustrated diagram of ethane to benzene process flow [16].

2.3. Process description of methane dehydroaromatization: non-oxidative process (NO-MDA)

Methane Dehydroaromatization (MDA) takes place under two conditions, which are the non-oxidative and oxidative conditions. Methane dehydroaromatization under non-oxidative conditions with a molybdenum loaded zeolite catalyst (Mo/HZSM-5) will produce hydrogen and aromatics compounds, mainly benzene [16]. However, there are a few chemical reactions that happen simultaneously in MDA such as the ethylene formation and carbonaceous deposit (coking).

The general overall equation is shown below [17]:

$$6CH_4 \leftrightarrow C_6H_6 + 9H_2 \tag{1}$$

Figure 2 shows the direct conversion of methane to benzene under non-oxidative conditions. Methane gas is fed and mixed with a recycle stream, which is rich in methane. The mixture is heated and maintained at 800 °C as it has to undergo an endothermic reaction in the dehydroaromatization reactor at 101.3 kPa and 800 °C [16]. The effluent of the reactor is fed to a membrane separator to continuously remove the produced hydrogen to overcome the limitations of low thermodynamic equilibrium of the conversion of methane. This could increase the conversion of methane to benzene. The remaining effluent is cooled and compressed later on. In order to recover the unreacted methane as an overhead product, the effluent is channelled to a flash separator.

The unreacted methane was recycled back to the process. A part of the stream was purged, and the remaining was sent back to the reactor. The liquid obtained as the bottom head product in the flash separator is sent to a distillation column. In the distillation column with operating temperature and the pressure of 100 °C and 2 bar, the benzene is purified and obtained as a top product. Naphthalene is obtained as the bottom product at the distillation column [18]. This process is assessed on the shale gas and there is yet to have any chemical plant that utilizes this process on benzene production. Since the composition of the shale gas and the associated gas is rather similar, this process will be considered as one of the processing pathways with relatively high novelty.

However, with the different components of the shale gas and the associated, the amount of the water present in the shale gas would be lower or none and this means that the benzene production from the shale gas can be neglected. However, for associated gas, the elimination of water is a crucial step to prevent pipelines corrosion or any unnecessary site reaction during the process [19].

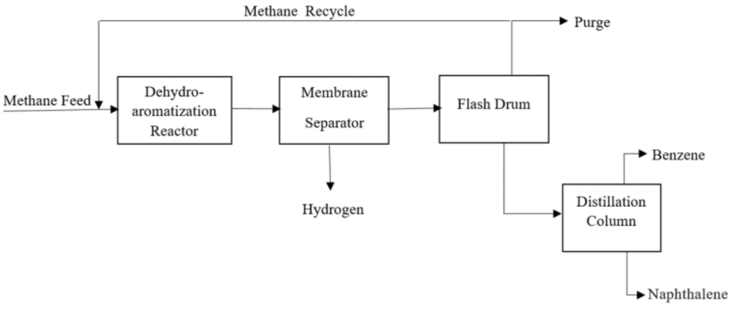

Fig. 2. Block diagram of Non-Oxidative Methane Dehydroaromatization (NO-MDA)[18].

2.4. Production of benzene from natural gas via Methanol Synthesis (MTB)

Many interests have been directed towards the natural gas recently as to produce valuable products from this domestic resource in Malaysia. Kent [20] explained that conversion of natural gas to methanol is a very common and commercialised method and about 4.5 million metric tons of methanol produced using this route in the United States [20]. After being converted to methanol, many other chemicals can be produced using methanol as the feedstock due to its versatility. Aromatics, which represent almost one-third of the market for commodity petrochemicals [21] are one of the valuable products many are looking into today. The main focus on the production of benzene through natural gas-to-methanol involves several significant steps as in Fig. 3.

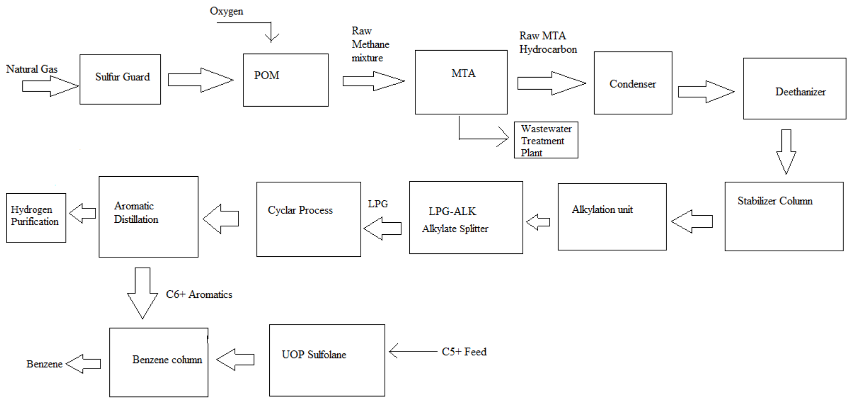

Fig. 3. Conversion of natural gas to benzene via methanol flow sheet [22].

2.4.1. Partial oxidation of methane (POM)

POM is a direct conversion pathway to produce methanol straight from methane with the presence of oxygen. Initially, the natural gas is being fed into a GTA (Gas-to-Aromatics) pipelines and passed over the sulphur guard to remove any unwanted mercaptan-based odorizes. Then, the desulfurized gas will pass through quartz lined high-pressure reactor at a temperature of 450 °C and pressure of 50 bar [22] undergoing a gas phase partial oxidation process. The single pass conversion of methane is 13% and the oxygen is being fed following the ratio of 63:30:6:1 to methanol: carbon monoxide: carbon dioxide: ethane [18].

Process reactions are shown as in Eqs. (2) and (3):

$$CH_4 + \frac{1}{2} O_2 \rightarrow CH_3OH \quad (2)$$

$$CH_4 + \frac{3}{2} O_2 \rightarrow CO + 2H_2O \quad (3)$$

2.4.2. Methanol-to-aromatics (MTA)

The effluent from POM, which is the raw methanol mixture will enter the Methanol-to-Aromatics (MTA) reactor passing over the catalyst, Ag/ZSM-5, which help to increase the overall selectivity at an operating temperature of 425 °C

[22]. The methanol is then converted to 44 wt% of hydrocarbons consist of C_5 aliphatic, light gases, LPG (liquefied petroleum gas) and 56 wt% of water [23]. The MTA-effluent is then later to be separated in the LPG-Aromatics separation section to further separate Liquefied Petroleum Gas (LPG) and aromatics product.

Process reactions:

$$\eta CH_3OH \rightarrow C_5H_{12} + \text{light gases} + \mu H_2O + \text{LPG} \quad (4)$$

where μ and η is the stoichiometry number of water and methanol respectively. The stoichiometry number is dependent on the amount of light gases and Liquefied Petroleum Gas (LPG) in this case.

2.4.3. Liquefied petroleum gas (LPG)-Aromatics separation

The upgrading of the MTA effluent is based on the National Renewable Energy Laboratory [24]. The separation of light hydrocarbons from the crude hydrocarbon mixture is done through the deethanizer while the light gases are being knocked out of the mixture first. The bottoms product of the deethanizer is channeled into the stabilizer column to remove any C_3 and C_4 gases, which later will be directed to the alkylation unit to be converted into isooctane [25]. The effluent is then passed through the LPG-ALK splitter, which will be separated out the LPG by-products.

Process reactions:

$$C_5H_{12} + \text{light gases} + \mu H_2O + \text{LPG} \rightarrow C_5H_{12} + \text{LPG} \quad (5)$$

2.4.4. LPG processing

Industrially, this process is also called the cyclar process. The LPG generated will be further processed in a reactor that used a metal promoted catalyst, Ga-based H-ZMS-5 to convert less valuable LPG to aromatics. The effluent will then be channelled into an aromatic distillation to separate the light gas and hydrogen-rich off gas from C_{6+} aromatics. The aromatics are then being further processed to produce desired and specific aromatic product, benzene [23].

Process reactions:

$$\text{LPG} \rightarrow C_6H_{14} \quad (6)$$

2.4.5. Aromatics complex

According to Niziolek et al. [26], to upgrade and separate the aromatics desired, the aromatic-rich hydrocarbon effluent produced earlier on in the MTA reactor, the C_5 aliphatic, enters the UOP Sulfolane process at 110 °C and 2.07 bar. The UOP Sulfolane process was first developed in 1960 and the aromatic complex in order to study the coproduction of liquid transportation fuels and aromatics from biomass and natural gas [27]. This process is used to recover the aromatics using tetrahydrothiophene 1,1-dioxide (Sulfolane) as the solvent. After that, following with a liquid-liquid extraction process together with an extractive distillation, about 99.9% of benzene is recovered with a mass purity of 99.8% [22]. The Benzene-rich distillate is condensed at 40 °C, which then resulted as an output of liquid benzene.

Process reaction:

$$2C_5H_{12}+\frac{1}{2}C_6H_{14}\rightarrow C_6H_6+C_7H_8+\frac{17}{2}H_2 \qquad (7)$$

This process has a proposed framework capable of producing 75% weight aromatics using domestically available natural gas. In terms of economic analysis, it is proven that from this framework the future chemical plant producing aromatics using this process is able to gain profit using in June 2015 prices [22]. However, the case studies are conducted only on aromatics such as para-, ortho-, and meta-xylene. Hence, applying this process to specifically producing benzene is yet to be further analysed. Additionally, this process has not been utilized in any chemical plant. Hence, this process is very favourable from the economic perspective. This is because of the market demand for benzene is high and the by-product (i.e., hydrogen gas) produced from this process can be sold at a favourable price as well.

2.5. Processes comparison and evaluation-production of benzene

The selection of the reaction pathway of production of benzene is based on the sustainability aspects. Economic Potential analysis is the first priority criteria when it comes to process selection. The processing pathway that gives the largest positive Economic Potential (EP) value will be chosen first, however, the final decision are also based on the environmental and safety aspects too. Table 3 shows the comparison table for all the reaction pathways of benzene production with the data collected regarding its economic, environmental and safety properties.

Table 3. Summary table of benzene production pathways.

Process	ETB	NO-MDA	MTB	References
Overall reaction	$3C_2H_6 \rightarrow C_6H_6 + 6H_2$ (direct conversion)	$6CH_4 \rightleftharpoons C_6H_6 + 9H_2$ (direct conversion)	$2C_5H_{12}+\frac{1}{2}C_6H_{14} \rightarrow C_6H_6+C_7H_8+\frac{17}{2}H_2$	[1, 2, 7]
Reactions involved	-	-	(1) $CH_4 + O_2 \rightarrow \eta CH_3OH + CO + \mu H_2O$ (2) $\eta CH_3OH \rightarrow C_5H_{12}$ + light gases + μH_2O + LPG (3)C_5H_{12} + light gases + μH_2O + LPG $\rightarrow C_5H_{12}$ + LPG (4) LPG $\rightarrow C_6H_{14}$ (5) $2C_5H_{12}+\frac{1}{2}C_6H_{14} \rightarrow C_6H_6 + C_7H_8+\frac{17}{2}H_2$	[4-6]
EP value	USD 1.79/kg benzene	USD 2.01/kg benzene	USD 1.13/kg benzene	
Temperature	600-650 °C	800 °C	40-425 °C	[4, 16, 22]
Pressure	1-20 bar	1.013 bar	2-50 bar	[4, 16, 22]
Capacity	500000 MTA	7143 MTA	32536 MTA	[20]
Yield	56.71%	91%	1.9%	[14, 17, 28]
Selectivity	67.68%	90%	22.8%	[14, 17, 28]
Conversion	46.6% to aromatics	16.7%	13%	[14, 17. 28]
Complexity	Medium	Low	High	
Type of process	Continuous	Continuous	Continuous	
Feedstocks	Fractional grade ethane	Methane	Methane and oxygen	[4, 18, 22]
By products	Hydrogen, propene, methane, ethylene, 1,3,5-trimethylbenzene	Naphthalene, hydrogen	Toluene and hydrogen gas	[4, 16, 22]
Safety concern	- High pressure. - High temperature, can ignite the	- High operating temperature.	- High operating temperature. - High pressure.	[29]

	hydrocarbons if oxygen is present. - Hydrocarbons in this process are volatile and flammable. - Hydrogen storage and transportation need to be handled with care.	- Methane gas is flammable and explosive.	- Solvent (sulfolane) used in aromatics complex reactions is toxic. - Methanol is flammable. - Hydrogen is explosive.	
Environmental impacts	- Consumes significant amount of energy. - Releases a significant amount of NOx and CO_2 emissions, which will need government permission. - Gaseous chemical needs to be scrubbed before releasing into the atmosphere.	- Naphthalene can cause pollution to the water as it is difficult to degrade. - Methane gas can cause global warming.	- Sulfolane can contaminate water and is detrimental to human health. - Methanol can contaminate water sources and processes strong odour.	[14]
Number of steps	3	1	5	
Advantages	- Low feedstock price. - Can obtain 99.6% purity of benzene. - Hydrogen produced can be profitable.	- High selectivity and yield. - No other reactants required. It can be reacted near or at methane sources. - MO/HZSM-5 permits high metal dispersion and shape selectivity.	- Product has high purity (reaching 99%). - By-products are valuable. - Profitable (only if the production is 5000 metric tonnes/day).	[30]
Disadvantages	- Average yield, selectivity and conversion. - Ethane is limited. - Release of carbon dioxide and produce thermal NOx by-products. - Consumes significant amount of energy. - Need to frequently replace the used catalyst.	- Serious catalyst deactivation. - Low conversion. - Consumes significant amount of energy.	- High operating cost due to high temperature and high pressure. - Low conversion and yield. - Process is complicated and involved many reactions.	[17]

2.5.1. Process economics and economic potential

Economic sustainability focus on the profitability of one process based on detail revenue (money earned by selling the products and incentives from government) and cost analysis (equipment cost, fixed cost, operating cost and other miscellaneous cost) as well as the payback period with its internal rate of return (IRR) throughout the process lifecycle. A process with high and good economic performance indicates a positive profit can be made for the company by choosing that process as their product line within its process life. The economic potential is not only based on the cost balance between the raw materials and products, but also as the design of the plant process goes on, however, the EP also has to consider the cost of equipment as well. According to Institute of Chemical Engineering (IChemE), the feasibility of the process based on its economic aspects can be affected by the process yield, process selectivity and its cost estimation [28]. Thus, only these three parameters will be considered in the preliminary evaluation of the processes of economic performance. The prices of the raw materials and product are listed in Table 4. By referring to Table 4, ETB as the lowest cost on its feedstock, which is USD 0.046/kg, followed by NO-MDA and the MTB process has the highest feedstock cost as its raw materials consist of methane and pentane.

As shown in Table 3, all three process pathways proved to have positive EP value and NO-MDA seemed to be as the most profitable process compared to the other two as it encounters the highest EP value, which is USD 2.01/kg of benzene. ETB has the second highest EP value, which is USD 1.79/kg of benzene and MTB has the least EP value, which only is USD 1.13/kg benzene. ETB and NO-MDA only differ about USD 0.36/kg of benzene, however, these two pathways are much higher (approximately more than USD 1.11/kg benzene) as compared to MTB.

From the environment and safety aspects, the following sections to further evaluate the feasibility of the processes are carried out.

Table 4. Prices of feedstocks and products.

Chemical name	Molecular formula	Cost (USD//kg)	Reference
Ethane	C_2H_6	0.046	[31]
Methane	CH_4	0.17	[32]
Pentane	C_5H_{12}	0.95	[33]
Hexane	C_6H_{14}	0.90	[34]
Benzene	C_6H_6	0.76	[35]
Hydrogen	H_2	6.50	[36]
Toluene	C_7H_8	0.60	[37]

2.5.2. Process selection based on environment aspect

The significance of the environment should not be neglected in the sustainability aspect. Pollutions should be avoided and taken care of because it is our responsibility to conserve and preserve our mother earth. Environmental-sustainability in-process production is focused on how to minimize waste (water, by-products, solids), and gas emissions. It is understandable that waste products are unavoidable, however, treatment processes should be implemented to ensure all the unwanted wastes have been managed well. Several indicators have been established by IChemE such as by-products generated, energy evaluation and renewability of the raw materials used to evaluate the sustainability of the process based on environmental aspect. The comparison is shown in Table 5 [36].

All the three processes emitted carbon dioxide to the surrounding. The ETB process is found to emit the largest amount of carbon dioxide to the atmosphere. Apart from that, ETB and MTB processes produce VOCs (Volatile Organic Compounds) to the atmosphere, which will cause pollution to the environment. However, the NO-MDA process only produces naphthalene as by-product beside carbon dioxide. Naphthalene produced has high market value, hence, it can be sold and utilized for other uses. Lastly, the MTB process will contribute a great amount of wastewater due to the use of sulfolane and the production of methanol as an intermediate product. In conclusion, the NO-MDA process has the least impact on the environment besides emitting carbon dioxide to the surrounding.

Table 5. Process comparison based on environmental aspect.

Process	Waste/by-products generated	Energy evaluation	Renewability of raw materials used
ETB	- Significant amount of carbon dioxide and NO_x are emitted to the surrounding. The gaseous emission should comply to Stack Gas Emission Standards from Environmental Quality (Clean Air) Regulations 1978 and Malaysian Air Quality Guidelines [38]. Hence, the chemicals in the gaseous state have to be scrubbed off first before emitting to the air. - 1, 3, 5 trimethylbenzene, propane and ethylene are VOCs (volatile organic compounds), which is toxic to aquatic organisms. [31-33] [38-40]. - Methane will absorb heat from sunlight and caused global warming. It is 84 times more potent than carbon dioxide [41, 42]. - Carbon dioxide emission is 4.98×10^{10} T/year [39].	- High consumption of energy due to high temperature and pressure [14]. - The highest temperature and pressure can reach up to 650 °C and 20 bar to increase the yield and conversion of the desired product.	- Ethane is a non-renewable hydrocarbon, which is less valuable as compared to other hydrocarbons and is always rejected through the pipelines [14].
NO-MDA	- Naphthalene is toxic and carcinogenic and being listed as a first-class pollutant by the United States Environmental Protection Agency [43]. -Naphthalene is highly stable thermodynamically and chemically, which make it a persistent pollutant. Hence, research to utilize bacteria to degrade this hydrocarbon to further reduce the pollution caused by naphthalene [44]. - Carbon dioxide emission is 0.44×10^5 T/year for capacity of 7143 MTA [16].	- High consumption of energy as well due to high operating temperature at 800 °C [16].	- Methane gas has the lowest density among all the hydrocarbons and it is the cleanest energy to combust. -Methane produces more energy per production of carbon dioxide. It causes a rise in temperature because it is a greenhouse gas.
MTB	- Toluene is an aromatic compound, which is highly volatile due to its high vapour pressure. It is also considered as a VOC and might form ground ozone that will affect the living organisms. - Carbon dioxide emission is 1.095×10^4 T/year for capacity of 32536 MTA [45]. - The wastewater produced during the MTA stage might contain traces of hydrocarbons and unconverted methanol [46] that can contaminate fresh water sources such as rivers and lakes. It	- High consumption of energy due to high operating temperature at 425 °C and operating pressure as high as 50 bar [22].	

	is crucial to implement a wastewater treatment plant to ensure the disposal of wastewater does not pollute the water sources. - Sulfolane is not volatile or being adsorbed to any matters when it is discharged to water or soil. Hence, biological treatment and in-site chemical oxidation are required to degrade the pollutant from contaminated water or soil [47].		

2.5.3. Process selection based on safety and health aspect

Safety is the utmost important factor that can lead to a sustainable process and long-term production. Having a conducive and safe environment to work in is significant to all the staffs and workers because everyone has their rights to stay safe and live a healthy life. According to United States Department of Labor [48], OSHA (Occupational Safety and Health Administration) prohibits employers from retaliating against workers for practising their rights. Hence, any identified hazards from chemicals that might be harmful to workers should be reconsidered and substitute chemicals that are less harmful. Therefore, Table 6 shows the comparison between three processes based on its safety and health aspect.

In term of safety, the ETB process is found to be the least safe process as the by-product produced has high flammability and also explosive. This is a dangerous working environment for the workers and staffs. Additionally, ETB process and MTB process are required to operate at high pressure. This can be dangerous and the equipment, which is operating at high pressure have to be utilized with extra care. As for NO-MDA and MTB processes, both processes produced toxic by-products. The by-products have to be handled with care. However, for the MTB process, a toxic chemical is involved to form benzene, which is the sulfolane. Hence, the NO-MDA process is much safer as compared to the other two processes.

Table 6. Safety comparison among the three processes.

Process	ETB	NO-MDA	MTB
Common aspects	1. All three processes required high operating temperature, which is above 400 °C. This may ease runaway reactions to occur and also the condition is difficult to control. Apart from that, at high temperature, ignition can easily occur if oxygen is present as hydrocarbons such as methane is highly flammable. Proper grounding and purging should be done to prevent static electricity or any possible ignition source to cause fire or explosion [47]. 2. Hydrogen gas is produced as a by-product. It is a highly explosive gas when exposed to oxygen, so it must be handled with care and store under specific conditions according to standard by OSHA 1910.103 [48]. 3. Desired product, benzene formed is toxic and volatile. Standard 1910.1028 [48] should be followed and PPE (personal protection equipment) have to be strictly equipped with workers and staffs who tend to expose to this substance. 4. Working environment is not very conducive because the part of the process is operating at high temperature, which causes heat loss and hot surrounding and also releasing unpleasant smell of product, which may lead to dizziness and nausea according to MSDS of benzene [45].		
Different aspects	- Operate at high pressure of 20 bar. Process is difficult to regulate and control. Process is difficult to regulate and control.	- Naphthalene as the by-product produced is classified as possible carcinogenic substances according to the	- Operate at high pressure of 50 bar. If there is any leakage in the reactor, explosion can occur very easily, which can cost lives.

	- By product 1,3,5-trimethylbenzene is a very flammable aromatic compound and is also explosive at 50 °C according to NIOSH [49]. Hence, this substance should be taken care of in terms of storage and transportation. - Ethylene (another by-product) is highly flammable and explosive as well according to its MSDS [50]. - Propene (by product) may form ozonide, which is already explosive at ambient temperature [51].	International Agency for Research on Cancer. - OSHA and NIOSH have both limited the exposure of 10 ppm at over an eight-hour time-weighted averagely to protect workers' health and safety during exposure in work.	- During aromatics complex process, sulfolane is used as the solvent for ions exchange reactions to form benzene [52]. However, sulfolane exhibit acute toxicity and should not be exposed in a very long period of time according to the MSDS [51]. Proper protection equipment should be applied on the workers for further protection and less exposure. - Toluene produced in this process is less toxic, however, long-term exposure of this substance can affect central nervous system according to OSHA [53].

2.6. Process selection and finalization

A decision matrix tool [54-56] is conducted to evaluate and finalize the most sustainable process pathway to be implemented for the benzene production based on the sustainability justifications that have been done. The decision matrix helps to analyse multi-criteria problem where all the criteria of the process will be accessed by a scoring scale of 1 to 3 whereby the process with the best performance based on the criteria will score the highest mark, 3 marks while the process that performed the least favourable will get the lowest mark.

Based on studies by EPA U.S. Environmental Protection Agency [57], the Economic Potential (EP) values is the only criterion to be considered in economic sustainability. According to the EP analysis, NO-MDA is the most profitable pathway as it has positive EP of USD 2.01/kg benzene-scored to 3, followed ETB, which obtained USD 1.79/kg benzene- scored to 2 and MTB only gained USD 1.13/kg [57] benzene in its EP analysis- scored to 1.

Yield and selectivity are two taken into consideration for the economic sustainability. According to the Table 3, the yield of NO-MDA is the highest among all (91%), followed by ETB (56.71%) and MTB has the lowest yield, which is only 1.9% of benzene being produced. Therefore, NO-MDA is given the score of 3 while ETB gained 2 and MTB get the lowest mark, which is 1 in terms of process yield. The selectivity of NO-MDA is the highest compared to another two (90%-100%)-scored to 3, followed by ETB (67.68%) scored to 2 and MTB (22.8%) is the least optimum process in term of selectivity-scored to 1.

In term of safety aspects, process conditions such as operating temperature is one of the indicators to ensure the working environment is safe for the employees. All three processes operate at high temperature (above 400℃)that can easily cause complexity to the process and may lead to runaway reactions and damage of equipment. MTB process operates at around 400 ℃ (lowest temperature as compared to others)-scored to 3, ETB operates at 600-650 ℃ [58] -scored to 2 and NO-MDA operates at the highest temperature among all (800 ℃), which give it the lowest score in term of process condition [59].

As for the operating pressure, NO-MDA operates at the lowest pressure (1.013 bar), which is closed to the atmospheric pressure and is able to prevent pressure leaking of flammable and toxic gas-scored to 3 while process of ETB and MTB are operating at high pressure, which may lead to difficulties in regulating the process and if there is any leakage in the reactor, explosion can occur easily -both scored to 1.

Apart from that, in terms of the chemical’s safety, as all three processes produce hydrogen gas as a by-product and hydrogen gas is highly explosive and it must be handled properly to avoid fire and explosion that can easily cause by ignition sources. In addition, these processes produce benzene, which is highly flammable and toxic chemical and can cause several health effects such as dizziness and nausea to a human being after a long period of exposure. Hence, all three processes get the same score of 1.

In accordance to environment perspective, renewability of the raw materials used for all three processes are non-renewable resources obtained from the natural gas. However, the raw material for NO-MDA and MTB has the cleanest energy to combust and it will produce more energy per production of carbon dioxide.

Hence, both of these processes receive a score of 2 while ETB scored to 1. In addition, energy consumption for all three processes are high due to high operating condition. Thus, three processes encountered the same score, which is 1. In terms of waste generation of the process, all three processes generate hazardous waste to the environment. However, the conversion rate of ETB is the highest, which minimized the by-product formation- scored to 3, followed by NO-MDA (conversion rate- 16.7%) is scored to 2 and MTB with a conversion rate of 13% is scored to 1.

In addition, the carbon dioxide emission according to EPA (Environmental Protection Agency) method, is also an environmental assessment of the impacts from the production of benzene. Let’s assume all the production capacity for the three processes is 500000 MTA. For the ETB process, the CO_2 emission is 4.98×10^{10} T/year [60]. It shows the highest of carbon dioxide emission among all the three processes, so it is given a score to 1.

As for NO-MDA, the carbon dioxide emission is the second lowest, which is 3.01×10^{6} T/year so it is given a score of 2 while for MTB, the carbon dioxide emission is 1.68×10^{5} T/year, which is the lowest so is given a score to 3 [61]. All the carbon dioxide emission is calculated based on the conversion of natural gas only and does not include other facilities. The decision matrix score sheet is shown in Table 7.

Table 7. Decision matrix of all three benzene processes.

Criteria	ETB	NO-MDA	MTB
Yield	3	5	1
EP analysis	3	5	1
Selectivity	3	5	1
Operating temperature	3	1	5
Operating pressure	1	5	1
Chemicals safety	1	1	1
Renewability of the raw materials	1	3	3
Energy consumption	1	1	1
Waste generation	5	3	1
CO_2 emission	1	2	3
Total score	**22**	**31**	**18**

Based on the decision matrix analysis, NO-MDA gained the highest score, which is 31 marks compared to the others. According to the detailed evaluation and justification, the process of NO-MDA is the most favourable process to be implemented for the benzene production. The highest score indicates that this process is sustainable in term of economic, safety and environmental perspectives

3. Conclusions

Benzene is an aromatic compound that has a growing demand for the past few years and is expecting to grow strongly for the years ahead. The new element that addressed in this article is to analyse an on-purpose build of the benzene production plant, which is economically viable. During process selection, three benzene process pathways are compared and analysed to select the best among all the three processes based on the economic, safety and environmental aspects. The sustainability of each process is evaluated by utilizing the decision matrix method. NO-MDA process is selected with the highest scores in the decision matrix method indicates that this process is the most sustainable one compared to the other two processes. Based on the economic aspect, the ETB has the highest EP value. Based on the social aspect refers to the community who live near the plant's area or the working personnel who constantly exposed to the chemicals, NO-MDA process operates at the lowest pressure among the processes that able to prevent leakage of gases during the process. Meanwhile, from the environment aspect, NO-MDA process provide the cleanest energy to combust and it produces more energy per production of carbon dioxide. From all three aspects, NO-MDA process can be concluded to be the most sustainable process among all the three processes.

Greek Symbols

η	Stoichiometry number of methanol
μ	Stoichiometry number of water

Abbreviations

BTX	Benzene, Toluene and P-Xylene
EP	Economic Potential
EPA	Environment Protection Agency
ETB	Benzene from Ethane
GTA	Gas to Aromatics
IChemE	Institute of Chemical Engineering
IRR	Internal Rate of Return
LPG	Liquefied Petroleum Gas
MSDS	Material Safety Data Sheet
MT	Million Tonnes
MTA	Methanol to Aromatics
MTA	Metric Tonnes Per Annum
MTB	Natural Gas Via Methanol Synthesis
NIOSH	National Institute of Occupational Safety and Health
NO-MDA	Methane Dehydroaromatization: Non-Oxidative Process
OSHA	Occupational Safety and Health Administration
PPE	Personal Protection Equipment
USD	United State Dollar
VOC$_S$	Volatile Organic Compounds

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