



## Indeginise Management Solution to Pakistan Excess Naphtha

**Author: Muhammad Fahad Khan (tomeetfahad@gmail.com), Dr. Nawar Khan**

Pakistan is gasoline deficit country (Platt's). Crude oil refineries in Pakistan are contributing 33.6 % to the country gasoline demand. Around a million metric ton of Naphtha i.e. raw material to produce gasoline was exported during financial year 2014-15, OCAC Pakistan Oil Report (2014-15). Naphtha could not be used as final product due to its lower octane number of 67(max) while the gasoline used in vehicles should have octane number of 87(min).

Countries with lower technology advancement opt to produce gasoline either by using blending techniques or by using different additives, Ivanova & Tsigankova, (2011). Russia, Ukraine, China and other countries where the industry does not provide sufficient production of high gasoline fractions are fulfilling their gasoline deficit by using Octane boosters. Technology advancement on the other side, especially in Pakistan, is not only time taking activity but is also an expensive option for crude oil refineries.

NMA, n- methyl aniline, is the non metallic additive and octane booster that is proposed to be used all over the country at a minimum percentage of 1.5 %. It will not only enhance the in-house gasoline production 95% but will also reduce Naphtha exports and gasoline imports. The paper discusses the impact of octane booster on petrol and naphtha market of Pakistan.

### BACKGROUND

During Financial year 2014-15, the crude oil refineries in the country had produced 1,591,439 M.Tons of gasoline. This includes Attock Refinery Ltd., BYCO Oil Petroleum Limited, BYCO Petroleum Pakistan Ltd., National Refinery Ltd., Pak Arab Refining Company and Pakistan Refinery Ltd with the Breakup given in Table-I,

Table-I, Refinery wise Gasoline Production							
Refinery Production (MT)	ARL	BPPL	BOPL	NRL	PRL	PARCO	TOTAL
	338,423	99,219	8,314	179,206	123,032	843,245	1,591,439

(Source: OCAC, Oil Report 2014-15)

The excess Naphtha produced during the same year was 1,008,261 M.Tons with the below mentioned breakup, Table-II;

Table-II, Refinery wise Production of Excess Naphtha							
Refinery Production (MT)	ARL	BPPL	BOPL	NRL	PRL	EPRF	TOTAL
	297,140	62,708	144,368	204,627	186,954	112,463	1,008,260

However the naphtha export and gasoline import figures for the financial year is reported as 997,964 M.Tons & 3,141,126 M.Tons respectively. Naphtha export is 66.29 % of total petroleum products exported during the financial year while PMG imported with total share of 24.84% excluding crude oil imports.

## SCOPE

To provide an indigenized management solution without any huge investment that could enable Pakistan for in-house utilization of export naphtha as gasoline.

## KEY WORDS

Naphtha, Gasoline, MMT, NMA, RON, Octane booster

## NOMENCLATURE

**NAPHTHA**, It is a primary component in the production of gasoline. It is used as a fuel feed to catalytic reforming for gasoline production and is the lighter component of atmospheric crude distillation unit extracted from the overhead drum of distillation tower; Nelson (1968) Naphtha is further processed to produce gasoline, generally known as petrol, Wauquier (1995)

**GASOLINE**, it is generally known as petrol and is a mixture of volatile liquid which is flammable in nature. It is hydrocarbon mixture obtained and extracted from petroleum. Petrol is used in internal-combustion engines as a fuel. Gasoline, is a preferred automobile fuel because of higher energy of combustion than any other component that could run an engine smooth.

It is produced from light volatile material called naphtha. Isomerization process is used for the conversion of straight-chain hydrocarbons (Naphtha) to branched-chain hydrocarbons with enhanced octane number, Arey & Earl (1961). Reforming process is also used to enhance octane number of naphtha. At a specific high temperature and in the presence of suitable catalyst the rearrangement of naphtha molecular structure is performed, Antos & Aitani (2004).

**MMT**, Methyl-cyclo-penta di-enyle manganese tri-carbonyl, the chemical has molecular formula of  $(CH_3C_5H_4) Mn (CO)_3$ , molecular weight of 218.1, flash point of 205 C and density of 1.38 g/cm<sup>3</sup>. Color of the chemical is varying from light clear yellow to yellowish brown. The chemical became popular after ban on tetra ethyl lead and is still in use at cost economical levels in various parts of the world as it was declared as safe to environment, engine and human.

**NMA**, n- methyl aniline, the chemical has chemical formula of  $C_7H_9N$ , molecular weight of 107.15, flash point of 78C and density of 0.989 g/cm<sup>3</sup>. Color of the chemical is varying from light clear yellow to yellowish brown and is in use as gasoline octane booster. It is blended in percentage and is considered as blending component.

**RON**, Research Octane Number, It determines petrol's resistance to pre-ignition, which not only causes knocking sound in the engine but could also damage engine in the long run. It may also be explained as the resistance of gasoline to detonation. The higher the Octane Number the better will be the engine performance and car would be fuel efficient.

**OCTANE BOOSTER**, any liquid, metal or chemical use to enhance octane number of gasoline either by dosage or by blending.

## INTRODUCTION AND LITERATURE REVIEW

Crude oil refineries around the globe are producing different petroleum products based on the type of installations they have. Yet the main product slate of a crude oil refinery through distillation techniques as per Nelson (1968) & Wauquier (1995) could be as;

LPG (liquefied petroleum gas)  
FBRN (full boiling range naphtha)  
Jet A-1 and Jp-8 (aviation fuels)  
KO (kerosene oil)  
HSD (high speed diesel)  
DFO (diesel fuel oil)  
FFO (furnace fuel oil)  
Lube oils or lube oil base  
Bitumen grades

Most of the products, even after its distillation from crude oil are not the final products. They need to be trimmed for further quality improvement either by processing it through other process unit or by addition of recommended chemicals within the predefined limits. The production sequence of the process to the disposal of the product along with the feedback for improvement from the last in cycle to the first in cycle is mentioned in generic production model, Khan (2008). The process flow diagram of distillation unit is as mentioned in Figure-I.

Uses of petroleum product likewise are; LPG (liquefied petroleum gas) domestic use or industrial use to get heat energy, naphtha is raw material to most of the petrochemical industry as well as to produce gasoline, kerosene oil has domestic use without any further treatment, aviation fuel has to be passed through necessary filtration and treatment section following by addition of approved additives. Diesel, after hydro desulfurization can be dispatched to market, furnace fuel oil can be sold into the market without any further treatment, same is the case with normal bitumen while lube oil has to be process through its own refinery, Green & Perry (1999). All products can be sold into a market subject to the requirement of specific market and or statutory defined specification for petroleum products. In Pakistan, the petroleum products have to be in compliance with PSQCA specifications. These specs are developed under guidance of ASTM, Euro and PSI specifications.

Production yield also play a vital role in economic evaluation of crude oil. It shows the total product slate along with its percentage production. Productions yields obtained from a distillation unit of Pakistan is given as in Table-III:

Table-III, Product yields from light sweet crude at Vacuum Distillation Unit

Crude Charge	7,080	Barrels
API Gravity	45.38	
Sp. Gravity	0.800	
Temperature (F)	60	
PRODUCTS	Barrels	Yields (%)
Liquefied petroleum gas	-	-
Naphtha	3,199	45.18
Kerosene	1,252	17.68
Diesel	1,853	26.17
Diesel fuel oil	125	1.77
Furnace fuel oil	512	7.23
Slop	2	0.03
Sub Total	6,943	98.07
GAS BALANCE		
HP Gas (Export)	124	1.75
FFO / Naphtha	12	0.16
Loss	1.0	0.01
Sub Total	137	100
Fuel & Loss	1.93%	

As naphtha is raw material to produce motor gasoline and it is typically having a lower octane number, ranging from 60 to 67, which is not able to be used as motor gasoline therefore crude oil refineries are using the state of the art technology that is naphtha catalytic reforming and light naphtha Isomerisation, Marshall (2015). These processes are in use to increase the octane number of naphtha and produce gasoline of >87 octane number to meet local specifications as mentioned in PSQCA specifications, Goldstein, et al., (2015).

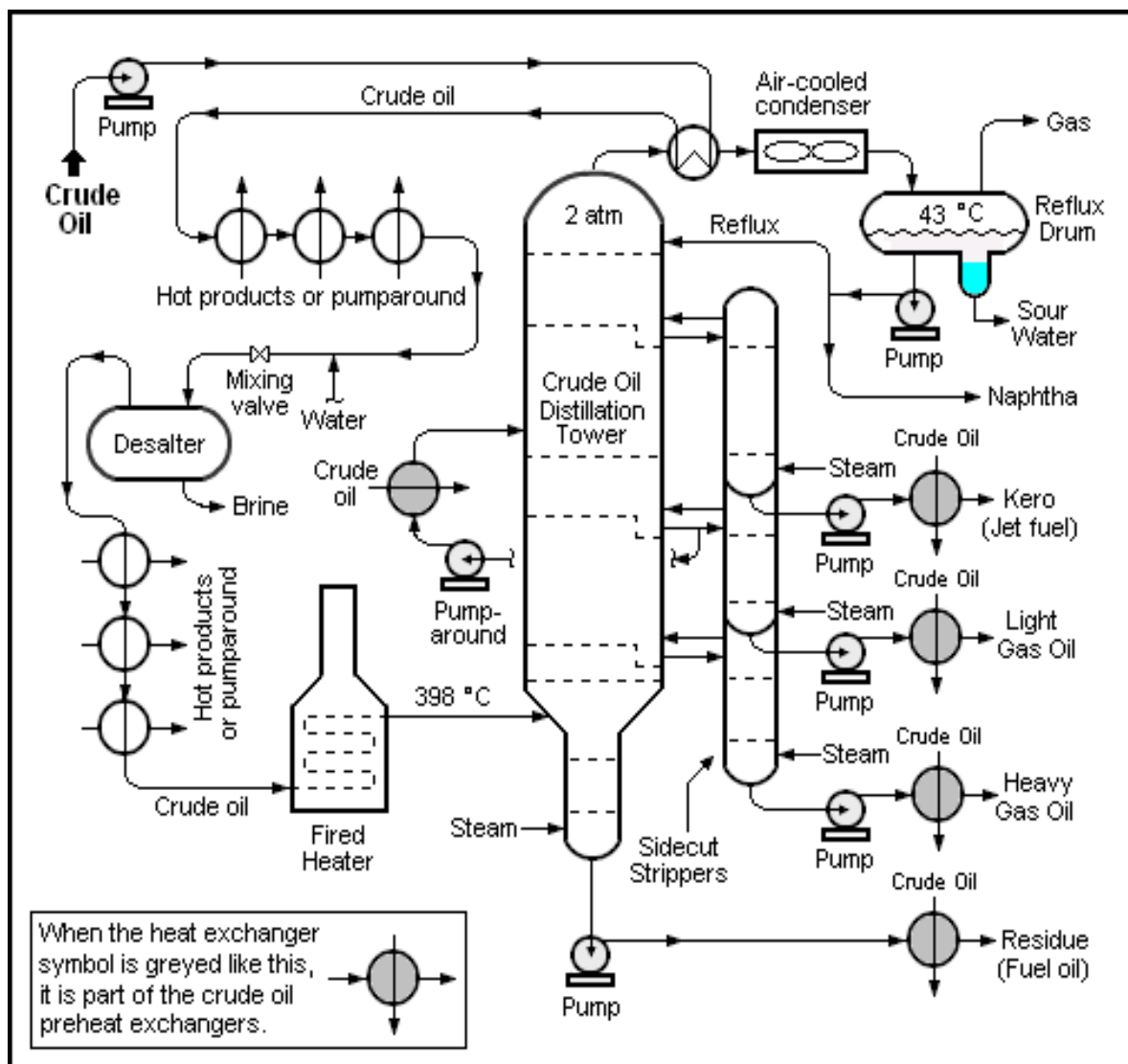


Figure- I, Process flow diagram (Crude Distillation unit) (Source: Milton Beychok)

After conversion through these units octane number of naphtha increases to 90+ at Reformer Unit, 87+ at Isomerisation Unit and 95+ at CCR, Continues catalyst regeneration. The PSQCA specification for octane number of gasoline in Pakistan is 87 in 2014-15.

The product obtained from reforming process may have constraint of high aromatics especially benzene that has limit of five (5) percent maximum. Moreover the product obtained from Isomerization process is having high vapor pressure issues and could not be sold direct to the market. Therefore most of the refineries blend the existing naphtha having a low octane with the product obtained from Isomerization and Reforming sections to increase the production of motor gasoline. Further to enhance gasoline production, some of the refineries are using organo-metallic base octane booster to blend their extra naphtha as per generic octane formula. The remaining naphtha needs to be exported. The projected import figures of PMG for the year 2015-16 provided by OCAC is 6,000,000 M.Tons, double the imports of 2014-15. This is also an indication of enhanced country requirement of gasoline.

The increased cost of producing the higher quality petrol is difficult for the refineries. MMT, an organo-metallic octane booster, is useful, efficient and cost effective for the refineries so it has to be permitted in petrol. It will allow the product to achieve the lower levels of aromatics, meeting Euro-IV specifications for gasoline. It will also cater the higher market demand of gasoline with improved octane number, DUNCAN (2000).

Use of n- methyl aniline improves overall engine performance by improving quality of gasoline. The major impact on quality of gasoline are improved stability of gasoline during transportation, decanting, filling and storages, reduction in vapor pressure of final blend, improvement in product specific gravity, reduction in fuel consumption due to vapor losses and good vehicle mileage, reduced exhaust emissions and reduction in maintenance of car, Rassadin, et al. (2006).

Ivanova & Tsigankova (2011), n-methyl aniline (NMA) an octane booster, is used in countries where the petrol producing industries don't have sufficient petrol production capacity to meet the high gasoline market demand. Some of the countries are using it to enhance high octane demand of their countries as well. Countries with lower technology advancement opt to produce gasoline either by using blending techniques or by using different additives.

Gasoline event report (2012), n-methyl aniline is in use for production of gasoline in countries including Russia, Belarus & Kazakhstan. It doesn't affect ecological characteristics of gasoline. The nitrogen oxides concentration in exhaust of a petrol engine due to NMA has negligible contribution. Due to timely investments on technology advancement, most of countries in the world don't have its production and application traditions. It has usage in rocket fuels where few of the countries have its production technology. In an expressed opinion, the use of MTBE (methyl tertiary butyl ether), Davidson & Creek, (2000) an octane booster, is explained to be more economical because the price of n methyl aniline in Russia is way too high comparing with MTBE.

Tretjakov (2013), TEL, tetraethyl lead, Studzinski, et al., (2001) a banned metallic octane booster was in use in motor gasoline. Due to carcinogenic nature of lead other organo metallic compounds and n-methyl aniline was introduced to meet gasoline octane deficit. They patented mainly in Russia, Ukraine, China and other countries where the industry does not provide sufficient production of high gasoline fractions. Despite of some unlikely comments both the organo metallic octane booster and n methyl aniline are still in use by oil traders and crude oil refineries around the globe due to its extended commercial benefits and negligible environmental impacts.

ATC113 (2013), N-methyl aniline is less effective than MMT (Methylcyclopentadienyl manganese tri carbonyl) and is typically used as a blending component for octane boosting at the rate of above 1.0 weight %. Reconfiguration of refinery to produce naturally high octane is suggested that could diminish the use of chemicals like n-methyl aniline, however the chemical possesses vast economical and commercial benefits.

ACFA (2014), use of n – methyl aniline can increase octane number but in parallel it will cause gum formation on engine at above 5.0% blending ratio that could damage the engine and shorten its life. The NTGA (nontraditional gasoline additive) has negative impact on all three major stakeholder i.e. human environment, engine life plus performance and human itself. The use of NTGA in china without following the predefined and allowed safe limits has not to be allowed, Gasoline Standard Directive (2013).

Developed countries are looking to regulate additives and chemicals used in petroleum products on the basis of environmental impacts and economical disadvantages. (USA, section 211, the Clean Air Act)

Albahri, et al. (2012), Chemicals and additives may be used to enhance octane number of gasoline. Due to potential hazard of chemicals, refineries are opting for technology advancement for production of high octane gasoline.

A chemical company has also claimed to develop a set of Octane boosters (including n-methyl aniline) for Petro bras, the 7th biggest energy company in the world. The quality of gasoline produced with chemical additives is also in compliance to the Brazil state standards for fuels. With the blending ratio of 1.5-2.5% of n- methyl aniline, the gasoline octane will improve by 6 points.

## DATA ANALYSIS:

The existing gasoline additive used in Pakistan has the capacity to increase octane number within range of 1.8 to 4.4 numbers with dosage rate of 18ppm to 54 ppm of manganese. Most of the refineries are using higher dosage rates to get maximum octane boost. Yet they are not succeeded to consume the total excess naphtha produced by the country and ultimately needs to export a good some quantity of naphtha.

NMA, N- Methyl Aniline (octane booster), having normal dosage rate of 2% - 5 % or lower could be introduced as possible option to reduce country wise export naphtha. It could not only be used as individual octane booster but is also compatible with existing organo-metallic octane boosters. With a dosage rate of minimum 1.0% ,the chemical is capable to enhance octane number of gasoline having base RON of 83 by 5.1 points while in combination with existing chemical with a dosage rate of 36 ppm of manganese and 1.0 % NMA, it boosts octane number of blend having base RON of 83.2 by 8.6 point, Table-IV.

Table-IV, Octane boost of NMA in gasoline, (Source: Refineries)

PMG Composition	Dosage	RON	PMG	Dosage Rate	RON	PMG
base	Rate	boost	RON		boost	RON
RON						
N-methyl	1.0	5.1	88.3	1.0 Vol% & 36	8.6	91.8
Aniline 99%	Vol%			ppm Mn*		

83.2	1.5	5.9	89.1	1.5 Vol% &	10.7	93.9
	Vol%			36 ppm Mn		

\* Organo metallic octane booster with manganese base

The secondary data gathered from OCAC, Oil Report-2014 is as;

Gasoline production	:	1,591,439 MT
Export Naphtha Production	:	1,008,260 MT
Gasoline Import	:	3,141,126 MT
Naphtha Export	:	997,964 MT

In order to calculate the impact of existing organo-metallic on Pakistan gasoline market we have assumed that all refineries are using manganese at injection rate of 36 ppm and use of 36 ppm manganese can enhance octane boost of gasoline by 3.2 points. The impact is reduction in gasoline by 270,500 MT thus without using any octane booster the country wise figures for both excess naphtha and 87 RON gasoline would be calculated as;

$$R = ((Ra * Qa) + (Rb * Qb) / (Qa + Qb)) + Rbc$$

Whereas;

Ra	RON of component "a"	65
Rb	RON of component "b"	87
Qa	Quantity of component "a"	?
Qb	Quantity of component "b"	1,591,439 MT
R	RON of Blend	87
Rbc	RON boost by Chemical	3.2

Calculating for "Qa" as;

$$87 = ((65 * Qa) + (87 * 1591439) / (Qa + 1591439)) + 3.2$$

Qa	Quantity of component "a"	270,500 MT
----	---------------------------	------------

Therefore, the total gasoline production and export naphtha without using any kind of gasoline octane enhancer calculated as;

Gasoline production	:	1,320,939 MT
Export Naphtha Production	:	1,278,760 MT

### Analysis of Gasoline & Naphtha with Octane Boosters

Analyzing the primary data tabulated in Table-IV, obtained from northern refinery of the country, the country wise gasoline and naphtha production by using formula  $R = ((Ra * Qa) + (Rb * Qb) / (Qa + Qb)) + Rbc$ , would be as mentioned in Table-V (gasoline and export naphtha with MMT & NMA).



Table- V, Gasoline and export naphtha with MMT & NMA

PMG				3,141,126 MT (Import)					
Detail	NMA	Mn	RON	PMG	Export Naphtha	PMG Enhance	PMG Enhance	PMG Import Reduce	Naphtha Export Reduce
Unit	V. %	ppm		MT	MT	MT	%	%	%
Calculated figures				1,320,939				1,278,760	
OCAC	0.0	36	3.2*	1,591,439	1,008,260	270,500	20.48	8.61	21.15
	1.0	0	5.1	1,718,939	880,760	398,000	30.13	12.67	31.12
	1.5	0	5.9	1,804,439	795,260	483,500	36.60	15.39	37.81
	1.0	36	8.6	2,167,939	431,760	847,000	64.12	26.96	66.24
	1.5	36	10.7	2,570,939	28,760	1,250,000	94.63	39.79	97.75
* theoretical octane boost with 36 ppm manganese									

Based on the figures of 2014-15 by addition of 1.5 % n methyl aniline with existing organo-metallic additive at injection rate of 36 ppm manganese the total gasoline produced would be 2.57 million MT. Hence the country wise production of gasoline would be increased by 20.69%. The total gasoline produced with in the country would be 54.32 %.

On the other hand, excess naphtha would be reduced to 0.6 % only. A significant reduction of 97.15% could be acquired.

The naphtha and gasoline figures after use of octane booster would be as,

Total gasoline consumption FY 2014-15	4,732,565 MT
In country production of gasoline	2,570,939 MT
Production of gasoline in Pakistan	54.32 %
Naphtha Export	28,260 MT
Naphtha export from the country	0.6 %

## CONCLUSION

Pakistan is gasoline deficit market with only 1.5 Million M. Tons of locally produced gasoline. A million M. Tons of naphtha is exported annually which needs to be converted into gasoline. The conversion of naphtha into gasoline could be done through installation of new process units with heavy investments which seems difficult for developing country like Pakistan. Moreover even if the oil producing companies manage to such investments, the process of installation and commissioning will take years to be implemented all over Pakistan. However the maximum installation required in case octane booster is blending and dosage equipment.

The use of both octane boosters will enable Pakistan to reduce its export by 97% and enhance in-house gasoline production by 94%. Moreover, the imports of gasoline would be reduced by 39%.

Some of the other improvements that it is capable to bring into the country are;

- Port congestion due to ships movement for import of gasoline and export of naphtha would be reduced.
- Cross country bowsters movement for transportation of export naphtha from one part of the region to another part could be reduced.
- Reduced movement of bowsters across the country for transportation of imported gasoline.
- Positive environmental impact on reduction of GHGs (green house gases) due to reduction in cross country bowsters movement.
- Demand for imported diesel to be reduced.
- Improvement in appreciation of Pakistani Rupee against dollar could also be an impact.

## RECOMMENDATION

In order to eliminate export naphtha from Pakistan by converting it into usable product i.e. petrol, it is recommended that n-methyl aniline with dosage rate of 1.5% along with existing organo-metallic octane booster with dosage rate of minimum 36 ppm should be regulated to be used by all refineries of Pakistan. The country should also search out for other suitable additives that could reduce fuel consumption and enhance engine performance.

Though the research is limited to production of gasoline from naphtha with octane boosters, other fuel additives that could enhance efficiency of engines should be study and explore in perspective of Pakistan. Effect of reduction in bowsters movement across the country and ships movement for carriage of fuel as a raw material and final product could be analyzed. Green house gases emissions under the research could be studied. Feasibility of product pipeline may also be area to be explored.

## REFERENCES

- Albahri, T.A., Riazi, M.R. and Alqattan, A.A., 2002. Octane number and aniline point of petroleum fuels. Fuel Chemistry Division Preprints, 47(2), p.710.
- Arey, J.W.F. and Earl, D.K., ExxonMobil Research and Engineering Co, 1961. Naphtha isomerization process. U.S. Patent 2,992,285.
- Antos, G.J. and Aitani, A.M. eds., 2004. Catalytic naphtha reforming, revised and expanded. CRC Press.
- ACFA, Asian clean fuel association, Report on harmful chemicals in gasoline blending, 2014.
- Davidson, J.M. and Creek, D.N., 2000. Using the gasoline additive MTBE in forensic environmental investigations. Environmental Forensics, 1(1), pp.31-36.
- Fuel Additives, use and benefits, September 2013/ATC113, A report by the additive technical committee Europe
- Green, D.W. and Perry, R.H., 1973. Perry's Chemical Engineers' Handbook/edición Don W. Green Robert H. Perry (No. C 660.28 P47 2008.).
- Gasoline event report 2012: the international gasoline 2012 conference, organized by Creon energy.
- Goldstein, S.S., Thurtoll, J.H., Kaul, B.K. and Marshall, G.A., ExxonMobil Research and Engineering Co, 2015. Catalytic reformer unit and unit operation. U.S. Patent 9,175,233.
- Ivanova, M.V. and Tsigankova, E.V., 2011. BENEFITS OF ADDITIVES USING IN OIL-REFINING INDUSTRY.
- Nelson, W.L., 1969. Petroleum refinery engineering. Series in chemical engineering.
- OCAC, Oil Report 2014-15, Refineries participation and share participation 2014-2015
- Studzinski, W.M., Valentine, J.N., Dorn, P., Campbell, T.G. and Liiva, P.M., Texaco Inc, 2001. High octane unleaded aviation gasolines. U.S. Patent 6,258,134.
- Total Quality Management (TQM), By Dr. Muhammad Nawar Khan, ISBN:978-969-8535-05-6, Publication, Date: 2005, Publisher: NUST, <http://www.ceme.nust.edu.pk/QMC/research/research.html>
- Rassadin, V.G., Shlygin, O.Y., Likhterova, N.M., Slavin, V.N. and Zharov, A.V., 2006. Problems in production of high-octane, unleaded automotive gasolines. Chemistry and technology of fuels and oils, 42(4), pp.235-242.
- Tretjakov, A.E., 2013. BENEFITS OF ADDITIVES USING IN OIL-REFINING INDUSTRY.
- Wauquier, J.P., 1995. Petroleum refining: crude oil, petroleum products, process flowsheets (Vol. 1). Editions Technip. Pg. No. 2, 271, 275, 382.