CHAPTER II

LITERATURE REVIEWS

Arsenic Compounds

Property of Arsenic Compounds: Arsenic is the third member of the nitrogen family of elements and hence possesses five electrons in the outer shell. Its properties are similar to phosphorous and antimony, with oxidation state of +3, +5, 0 and -3. The element exists in several allotropic forms. The most common is a grey, crystalline material with low heat and electrical conductivity. Condensation from vapour produces a black form which is converted to the grey by heating to $360^\circ C$. Arsenic melts at $817^\circ C$ under 28 atm of pressure but sublimes at $613^\circ C$ under normal pressure. Arsenic compounds have numerous practical application. As shown in Table 2.1, pesticides represent by far the largest commercial use of arsenic compounds.

Toxicity of Arsenic Compounds: There is an extreamly wide variation in the toxicity of arsenic and its organic and inorganic compounds. Elemental arsenic has a relatively low level of toxicity. However, continued exposure to elemental arsenic dust can caused toxicity problems (Meketta, 1979). The toxicity of arsenic compounds is the highest when the element is in the trivalent state. Trivalent arsenical combine with SH and SeH groups, causing inactivation of enzymes

containing these groups. Compounds of pentavalent arsenic are less toxic because they show reduced activity on enzymes. In general, pentavalent organic arsenicals are less toxic than pentavalent inorganic arsenicals. Elemental arsenic and several of its compounds are specifically classified as Hazardous Materials (Graziano, 1974). The maximum aceptable concentration for an 8-h exposure to arsenic compounds is 0.5 mg arsenic (elemental) per cubic meter of air (National Safety Council Data Sheet, 1961)

Table 2.1   Commercial Uses of Arsenic Compounds in 1974
            (Kirt Ottmer, 1975)

Use	Metric tons	%
pesticides	34,000	65
wood preservation	9,500	18
glass	5,000	10
alloys and electronic	1,500	3
miscellaneous	1,000	4

Characterization and Identification of Arsenic in Petroleum

In order to improve arsenic removal methodology, a good understanding of the nature of the arsenic species present is clearly desirable. Arsenic is usually found in petroleum, crude oil and shale oil. The concentration

of arsenic in these hydrocarbons often exceeds 20 ppm, with value typically ranging from 0.111-0.263 ppm for petroleum (Fish and Brinckman, 1983), from 20 to 80 ppm for full range shale oil derived from Colorado oil shale and from 20 to 1200 ppm for many coal tar distillates (Albertson, 1984). Table 2.1 represents arsenic levels normally encountere in sereral oils (Carr and Stahlfeld, 1985).

Table 2.2 Representing of arsenic content in petroleum (Child, 1986)

Oil sample	Arsenic content (ppb)
Deasphalted oil	205
West Texas coker gas oil	187
Low-sulfur coker gas oil	140
Ordovician heavy vac. gas oil	128
Grand Bay mix hvy. vac. gas oil	199
Misc. source(Delta mix) hvy. vac. gas oil	372
West Texas hvy. vac. gas oil	213

Arsenic compounds are distributed throughout the boiling range of petroleum (Petterson et al.,1987). It can form many volatile compounds such as arsenic sulfides and arsine (Fox et al.,1977). Subsequent reactions with pyrolysis hydrocarbons lead to the formation of various types of arsenic compounds including: arsenate, phenylarsonic acid and neutral organic arsenic compounds such as trialkylarsine oxide (Weiss et al., 1981).

However, complete analysis of the arsenic compounds in shale oil is not yet available at the present time. However the nature of arsenic contained in petroleum is not completely understood, the previous study suggests that arsenic in crude oil is in organometallic and inorganic forms (Goyal, 1988). Figure 2.1. shows the distribution of arsenic compounds found in condensate.
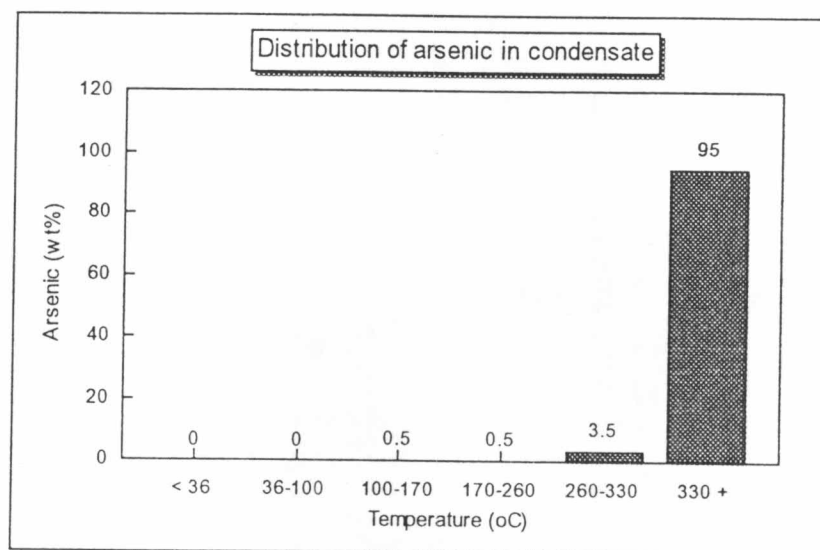

Figure 2.1. shows the distribution of arsenic compounds found in condensate.

Organic Arsenic Compounds: Acid organoarsenic compounds such as methylarsonic acid and phenylarsonic acid were found in oil shale retorting products (Fish et al., 1982; Weiss et al.,1981). These studies were confirmed by Fish and Brinckman (1983) who have coupled a graphite furnace atomic absorption spectrometer (GFAA) to a high performance liquid chromatograph (HPLC) to analyse arsenic compounds in oil shale. Neutral

organoarsenic such as arsine and alkylarsine derivatives were also identified as one of the arsenic compounds in light hydrocarbon and natural gas by gas chromatography mass spectrometry (Irgolic et al., 1990).

Inorganic Arsenic Compounds: Inorganic arsenic is usally present in crude oil. Arsenate(AsO_4^{3-}) was found in oil shale retorting products(Fish et al., 1982, Weiss et al., 1981 and Fish et al., 1983). Other arsenic compounds may also be present in the petroleum such as arsenate, arsenite and arsenic oxide (Delaney, 1988)

Study of Catalyst Poisoning by Arsenic Compounds

The 'life' of a catalyst may be defined as the period during which the catalyst produces the required product equal to that originally specified. For most catalysts the activity declines sharply at first and then decreases much more slowly with time. Earlier work on the poisoning of metallic catalysts was brought together by Maxted (1951). In this he proposed a theory of catalyst poisoning based on the electron structural properties of the poison and the metal catalyst. The concept employed is that the poison is adsorbed on the active metal sites to form a chemisorbed complex. Metallic catalysts susceptible to poisoning are confined mainly to metals of Group VIII and IB of the periodic table. These are listed in Table 2.3. Most of metals are employed for hydrotreating and reforming reactions.

Table 2.3 Catlytic metals most susceptible to poisoning.

Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

The principal poisons that are effective in deactivating these metal catalysts belong to the following groups:

(a) Molecules containing elements of the periodic table Groups VB and VIB, i.e. N, P, As.

(b) Compounds of a large number of catalytically toxic metals

(c) Molecules containing multiple bonds, such as CO, and strongly adsorbed organic molecules.

The toxicity of the compounds of Group VB was attributed by Maxted to the presence of unshared electron pairs which facilated the chemisorption process. Arsenic is element of Group VB of the periodic table. Arsenic poisoning of catalyst, particularly reforming and hydrotreating, is a long standing problem. Several techniques have been used to clarify the nature of arsenic poisoning on catalysts. X-ray photoelectron spectroscopy (XPS) and Mossbauer emisssion spectroscopy (MES) have used to study the state of arsenic on $Co-Mo/Al_2O_3$ and Mo/Al_2O_3 catalysts. It indicated zero valent and trivalent forms of arsenic present on the Mo/Al_2O_3 catalyst in hydrodesulfurization process (Merryfield et al.,1984). Ng (1991) investigated the

adsorption of arsine on Ni/SiO2 by hydrogen chemisorption method. He observed that arsine can attack many layers of a nickel catalyst at room temperature. At top layer of nickel atom, the chemical state of arsine was probably boned to three nickel sites.

The effect of arsenic on catalyst has been investigated and reported. Merryfield et al. (1984) studied the effects of arsenic on $Co-Mo/Al_2O_3$ and Mo/Al_2O_3 catalysts in hydrodesulfurization. These catalysts were tested for hydrodesulfurization activity with and without arsenic content. It showed that 3.6% arsenic on catalyst alomost completely deactivates the catalyst. The small amount of activity remaining was that expected for Al_2O_3 alone.

Further studies of hydrodenitrogenation reaction was reported by Hisamitsu et al.(1987) and , they studied rate of catalyst deactivation in the presence of $Ni-Mo/Al_2O_3$ catalyst. This study was compared between shale oil with and without adding arsenic. Catalyst deactivation was significantly accelerated by adding 30 ppm of triphenylarsine(Ph3As). Gutberlet (1988) studied the effects of arsenic on DENOX catalyst in denitration process. After a 400-hour operation, the activity of catalyst was decreased by 65 %.

From the previous literature survey, we can point out that the present of arsenic in petroleum is the result of catalyst posoining. Catalyst deactivation by arsenic may result from ;

(a) chemical poisoning, as arsenic compounds adsorb on catalytic sites or react to form other strongly adsorbed species

(b) physical blockage of the catalyst surface, preventing access of reactants to the catalytic sites

(c) physical blockage of catalyst pore(or pore mounths), preventing access of reactants to interior pore volume.

Studies of Arsenic Compounds Removing from Petroleum

As state previously, three main methods are currently employed, namely thermal treatment, chemical treatment and adsorption on inorganic material. Thermal treatment provides a heat treating step for converting arsenic to solid form. After that treated feedstock is separated from the solid to recovery a product having a reduced arsenic content. Chemical treatment is a process for removing arsenic with an oxidizing agent to convert a portion of arsenic to more water-soluble form. Adsortion currently the most widely used method on an industrial scale. It gives a process for removing arsenic by contacting feedstock with an adsorbent. Arsenic will be deposited on adsorbent due to interaction between arsenic and adsorbent. In this section, each of the methods will be studied, compared and decided to find the best method, to remove arsenic from petroleum.

Thermal Treatment

Thermal treatment is a method which has been developed initially for arsenic removal. This method is conducted by heating feedstock at the optimum temperature for a time. Thermal, which taken to feedstock, will change the properties of arsenic. This causes arsenic compounds to produced the 'precipitate' that is removed from feedstock. The term 'precipitate' is referred to any solid or tarry materials that can be separate from feedstock by physical separation. Pioneering work in this field was done by Curtin (1977), who investigated a method of removing arsenic contaminants from hydrocarbonaceous fluid such as synthetic crude oil and fraction thereof. This process was carried out by passing shale oil to the reactor. Then, the reactor was pressurized with hydrogen at 1,675 psi and heated to a temperature of 801 oF for 27.7 minutes. Arsenic in shale oil would be convert to solid form. Following the heat treating step, treated shale oil was separated from the mixture by filtering or centrifuging. Untreated and treated shale oil were found to contain 17.4 and 2 ppm of arsenic, respectively.

Rhodes et al. (1985) purposed an improved process for the removal of arsenic from shale oil. Their studies were similar to Curtin's method but they operated in a reducing atmosphere. Shale oil was fed into a reaction vessel at a temperature about 250°C. After 15 minutes and in hydrogen environment, the properties of arsenic were be changed. It caused arsenic in shale oil to produce

solid form. Hence, it was found that the concentration of arsenic in product is less than 1 ppm.

The above-mentioned processes are thermal treating which heating the petroleum in a period of time to form a suspended precipitate and subsequently separated by physical method. The problems of these processes are low efficiency, take a long time, costly performance and installing expensive filtration or centrifuging. For the reasons, this method is not served to remove arsenic from petroleum. Accordingly, it is important that the other methods be still desired.

Chemical Treatment

The second method is used chemical substance for converting a portion of arsenic to more water-extractable form. Chemical substance will break the molecular bond into a form which is more soluble in water than in feedstock. The converted arsenic compounds are then separated by water extraction or water leaching. It is similar to the first method, but using chemical substance instead of thermal.

Many types of chemicals have been thoroughly reviewed in several papers, for example, oil-soluble metals (Young,1977). It used by blending the metal with shale oil. In his study, nickle naphthanate was blended with crude shale oil containing 50 ppm of arsenic. The mixture solution was placed in an autoclave that was subsequently pressurized with hydrogen at 110 psig. Heating at a temperature about 650 oF and carrying out for 2-3 hours could convert at least some of arsenic to

water-soluble form that existed as an undissolved solid. The mixture was filter and then analyzed for arsenic. It was found that the concentration of arsenic in product was decreased from 50 ppm to 15 ppm. Albertson (1984) provided a process for reducing the arsenic content in shale oil. In his experiment, 30 grams of elemental sulfur was blended with 50 ml of raw shale oil and the mixture was held at 150 oF for 5 minutes. After filtration, the product hydrocarbon contained 5.5 ppm of arsenic, indicative of an 88.8% arsenic reduction.

Fenton (1985) used aqueous solution containing sulfur compounds in arsenic removal, such as hydrogen sulfide. A retorted shale oil containing 50 ppm of arsenic was treated with an aqueous solution and pressurized with 25 psi hydrogen sulfide at 200°C. The arsenic content was decrease to 10-30 ppm. Many sodium compounds have been used for decreasing the concentration of arsenic in hydrocarbon. The similar experiment was studied by Yakovleva (1987). In this experiment, sodium hydroxide solution was used for leaching of arsenic from antimony dust. The reactant, containing 5-10 ppm of arsenic, was leaching with sodium hydroxide solution at 90°C for 0.5 hour. This process was successfully to remove arsenic more than 98%.

In addition to using of sodium hydroxide, sodium chloride solution was also used for removing arsenic from exhaust gas. Taura (1980) investigated the arsenic removal by passing the exhaust gas, containing 10,000 ppm of arsenic, through the adsorbing column. Arsenic in exhaust gas was contacted with sodium chloride to make

the concentration of arsenic be less than 0.05 ppm. Due
to effective performance in gaseous phase, the oxidizing
agent solution might be converted to oxidizing layer.
The method described above was arsenic removal by
converting arsenic form and adsorbing on oxidizing layer.
Therefore, the investigators of Mitsubishi Rayon Co.,Ltd.
(1985) used potassium permanganate and nitrate acid as
oxidizing layer. Thus, a gas containing arsine (0.1 mg as
arsenic) was bubbled in a test tube containing oxidizing
agent. As a result, the arsenic adsorbed was 0.093 mg.

Elemental sulfur or aqueous solution hydrogen
phosphate is useful in the treatment of shale oil and
other synthetic oil, containing relative large
concentrations of arsenic. Another chemical, which
above-mentioned, such as chloride or iron compounds could
be used for converting arsenic to water-soluble form.
For this reason, Arakawa (1988) studied the method to
remove arsenic from petroleum fraction by passing the
petroleum to contact with iron ion. The petroleum
fraction in this study is particularly preferred 4C or
lower hydrocarbon. Such petroleum was treated by
contacting with 5% ferric nitrate solution at 25-100°C for
5-200 minutes, or sufficient time enough to remove
arsenic impurities. After that the arsenic content in
petroleum was decreased to be less than 10 ppm. Delany
(1988) used the chloride compounds, such as hydrochloric
acid or phosphorus trichloride, as the oxidizing agents.
For example, hydrochloric acid was chosen to mix with
shale oil containing 31 ppm of arsenic in autoclave. The
resulting mixture was typically mixed with water and

separated into a product and water phase. The process was carried on 2 hours at the temperature and pressure of 338oF and 400 psi, respectively. The arsenic concentration was decreased to 5.55 ppm.

Although a chemical treating method can achieve higher percentage of removal, but it cannot reach the concentration of arsenic to a level of part per billion. These processes, however, are relatively expensive and cause a substantial amount of feedstock to be lost to the water phase. Chemical substances which used present a problem to the disposal of water phase and cause equipment corrosion.

Adsorption

The term "adsorption" is used to describe whatever mechanism, including absorption, adsorption, deposition, chemical reaction, etc., by which the arsenic is removed and retained on adsorbent materials. The removal of arsenic by adsorbent is generally carried out the same way for removal of metal contaminants. It depends on the nature of feedstock, the properties of arsenic, the oeperating condition and the nature of the adsorbent (Young, 1977). Force-interaction between arsenic and adsorbent are considered to be the important factor. Under actual condition arsenic will be contacted on active site of the adsorbent. If interaction between arsenic and adsorbent is strong, arsenic would be adsorbed and retained on a surface of adsorbent to form the stable compounds. If interaction is weak, arsenic

will pass through the adsorbent without adsorbing or retaining on adsorbent.

The removal of arsenic by adsorption method have fulfilled in both vapor and liquid fractions. This section would like to discuss the removal of arsenic in vapor phase separating from the removal of arsenic in liquid phase in order to make a distinction between the two. It should be recognizing that the two processes are often unrelated, or related, or overlapping.

Most of adsorbents, useful in vapor fraction, comprise metal oxides on support such as alumina or silica. Kagaku and Kitagawa (1982) used copper oxide or manganese oxide as the adsorbents for adsorbing arsine. Hydrocarbon, containing arsine or arsine derivatives was brought into contact with adsorbents in vapour phase. The amount of the arsenic compounds were reacted and adsorbed on adsorbent. This process did not necessary the pretreament other than vaporization of hydrocarbon. Three years later, Carr et al. (1985) used copper oxide and lead oxide on alumina support as the adsorbent to remove arsenic compounds in vapour fraction of petroleum. The operating conditions was operated at the temperature about 150-250 oF and at pressure about 250-300 psig. The removal of arsine by Cu/Al_2O_3 was almost 100% when the initial concentration of arsine was 1000 ppb. It is believed that arsine is reacted with copper oxide and adsorbed on support as following:

$$3CuO + 2AsH_3 \ \text{-----------} \rightarrow \ Cu_3As + As + 3H_2O$$
$$3CuO + 2AsH_3 \ \text{-----------} \rightarrow \ 3Cu + 2As + 3H_2O$$

Other metals can be used as adsorbents, for example, zinc or maganese in order to increase the efficiency of arsenic removal. Copper and zinc oxide, as the adsorbent, was studied by Nowack and Johnson (1986). The adsorbents could be employed in various processes, depending upon the nature of the feedstock. It was believed that some chemical reactions take place between the arsenic and the adsorbent as the following occur:

$$3Cu(CrO2)2 + 2AsH3 \text{ ---------> } Cu3As2 + 3Cr2O3 + 3H2O$$

The results showed that 5.5 grams of arsenic were adsorbed on 27.94 grams of adsorbent. Johnson Nowack (1986) used adsorbent to reduce arsenic from gaseous streams of hydrocarbon, by contacting such streams with a mixed metal oxide adsorbent. The adsorbent composition useful in this study comprised copper and zinc oxide on alumina support. This process was carried out by passing through a stainless steel tube reactor. The reactor was packed with an inch middle layer of the adsorbent material and a 5 inch top layer of glass beads. The gas streams containing about 10-25 ppb arsenic, as arsine, was passed through the reactor tube containing the oxidized copper and zinc oxide adsorbent material. The reaction temperature was about 95°C, and the gas feed rate about 95 l/hr. The exiting gas stream was first allowed to bubble through two traps in series, each containing silver diethyl dithiocarbamate in pyridine and aqueous hydrochloric acid. After about 1 month on stream, no arsine break through had occurred. The treated product

gas contained less than 0.7 ppb of arsine and weight of
arsine on adsorbent was 3.48 x10-3 grams per 58.5 grams
of copper-zinc oxide adsorbent.

Ichikawa et al. (1987) invented the process for
removing arsenic from petroleum. The process comprised
the step of contacting the arsenic containing petroleum
fraction with a sulfurized adsorbent. The sulfurized
adsorbent was prepared by reacting of activated carbon,
bituminous coal or an organic polymer with a sulfur
compound to obtain a mercapto group. Thus, a light
naphtha, containing 220 ppb of arsenic, was contacted
with sulfurized adsorbent at 0-100°C and 5 h-1 LHSV,
resulting in removal of more than 99% arsenic from the
naphtha. Miyazawa et al. (1988) prepared an adsorbent
for removing arsenic compounds from flue gas. To prepare
an adsorbent by impregnation with aqueous nitrate
solution on mordenite and clay, since an adsorbent
contained nickel and nickel oxide 14% by weight. An
adsorbent was introduced together with the gas,
containing vapour of As2O3, into a reactor zone.
Temperature of operation was maintained at 350°C, when the
gas flow rate and adsorbent were 2 litre per minute and 2
grams per minute, respectively. In the reactor zone, the
As_2O_3 vapour was passed through the adsorbent and reacted
with each other. After a predetermined interval of time,
the adsorbent was collected and the unreacted As_2O_3 vapour
was discharged through the collecting zone. This
experiment showed that the adsorption ratio was 26%.
Roussel et al. (1988) improved a process for reducing the
arsenic content in hydrocarbonaceous oil by contacting

with a Ni, Co, Fe,and/or Pd containing catalyst. This operation was carried out at the range of temperature about 130-175°C and pressure about 1-50 bar. Thus after, the refined product contained arsenic content less than 1 ppm.

Arsine was always found in liquefied hydrocarbon and made a major problem in hydrotreating process. Alkali earth metal compounds were such metal used to remove arsenic containing from hydrocarbon. The removal of arsenic is better efficiently by incorporating at least one kind of alkali earth metal compounds such as nitrate or chloride of Mg, Ca, Sr or Ba and molecular sieves. Arsenic was removed from combustion gas by mixing with the above agents (Rikimaru et al.,1988). The operation was left 5 hour at 500 °C to adsorb 59.1% of arsine.

Nojima et al.(1988) invented the process for preventing the denitration catalyst from arsenic poisoning. The raw feed gas contained arsenic compounds, such as As_2O_3, was contacted with a zeolite Y adsorbent for decreasing the arsenic content. In the process of a denitration catalyst, a coal-fired boiler flue gas was decreased the arsenic content from 7.3 ppm to more than or equally to 0.4 ppm. After operation for 200 hours, the denitration catalyst remained at 90% efficiency versus less than 80% for a control without removing the arsenic compounds. Debras and Bodart (1989) investigated the method for removing arsenic compounds such as arsine. To remove the arsine, light olefin was passed over an adsorbent comprising nickel oxide deposited on a support

material. Thus, a liquid hydrocarbon feedstock containing C3H6 99.5% and residual arsine 150,000 ppb was passed over an adsorbent. The used adsorbent was consisted of 43.4% of silica-alumina support and 49% deposited 0.688:1 Ni/NiO. The operating condition was carried out at the temperature and pressure of $25°C$ and 1.5 MPa, respectively. The results to give a purified feedstock with arsine content were less than 50 ppb at the first 24 hours of operation.

Cull et al.(1990) studied the rejuvenation of metal oxide after adsorbing arsenic compounds from hydrocarbon. The experiment of this study was performed in the vapour phase metal oxide, used as catalyst. One tenth gram of a catalyst having a composition of about 40-40-20 of $CuO-Zn-Al_2O_3$ was contacted with a stream of nitrogen containing 20 ppm arsine. The catalyst adsorbed about 19.4% arsenic before arsine breakthrough occurred. Mean while, the catalyst having a composition of about 20% PbO on alumina adsorbed about 3.04% arsenic. This study might conclude that CuO-ZnO catalyst has a better advantage to use in arsenic removal.

Nowack et al. (1991) provided a process for at least partially removing trialkylarsine from a liquid hydrocarbon. Generally, this hydrocarbon comprised methan, ethane, ethylene, propane, propylene, n-butane, isobutane, butene and the like. The process comprised the step of contacting a fluid feed that contained at least one trialkyl arsine with a solid adsorbent. When trimethyl arsine breakthrough occurred (i.e., when the adsorbent had reached its maximum arsine adsorption

capacity) the adsorbent was weight. The different
between this weight and the initial weight of fresh
adsorbent was the weight of adsorbed trimethylarsine.
The following adsorbent materials in this study were
tested, as following;

(1) a commercial Hopcalite having the approximate
chemical formula of CuO-MnO$_2$ comprising about 50 weight
percent of manganese, about 12 weight percent of copper
and 0.3 weight percent of sodium) ;

(2) CuO/ZnO(providing by BASF Wyandotte
Corporation, Parippany, N.J.) ;

(3) Cu(II)chromite(providing by United Catalyst,
Inc., Louisville, Ky.

The results of testing were summarized as following ;

adsorbent	millimoles Trimethyl Arsine Adsorbed per gram
Hopcalite	0.60
CuO/ZnO	0.00
Copper (II) chromite	0.00

The results showed that Hopcalite adsorbed
trimethylarsine while two other copper oxide-containing
materials were not effective as trimethyarsine
adsorbents.

Arsenic compounds in liquefied petroleum has many
types other than gaseous petroleum. Thus, The degree of
arsenic removal in liquefied feedstock will decline
comparatively to arsenic removal in gaseous feedstock.

Generally speaking, any arsenation catalyst
(arsenic-removing adsorbent) may be used in restriction.
Several catalysts were tested to determined the relative
usefulness for removing arsenic content from petroleum.
A wide variety of suitable adsorbents are tested for
dearsenation activity such as nickel, molybdenum, cobalt,
copper and silver having alumina, silica and the like as
supportors. Typically, the dearsenation process is
conducted at temperature less than $1000°F$ and pressure of
from 0-1500 psi.

The prior art suggested several studies for
removing arsenic. Young (1977) used $NiO\text{-}MoO/Al_2O_3$ as the
catalytic absorbent to remove arsenic in shale oil. The
absorbent was presulfided before operation. It was then
contacted at temperature of 650 $°F$ and a pressure of 200
psi with Colorado crude shale oil containing 720 ppm
arsenic (as arsenic trioxide). During the first 4.1 days
of run, the product oil composition did not exceed 2.0
ppm arsenic. Sillivan (1979) disclosed a method of
avoiding feed-transfer-line plugging by a deposit
comprising arsenic in hydrocarbon. In this method, a
mixture of hydrogen gas and the oil was formed in situ in
a bed of porous particulate contacting material. The
porous contacting material had surface area more than 290
m^2/g, a pore volume of at least about 0.44 cc/g and the
composition as following:

component	weight
NiO	10
WO3	25
SiO2	27
Al2O3	30
TiO2	8

The hydrocarbon oil mixed with hydrogen, contacting under arsenic-removing condition, including temperature in the range of about 315°C to 480°C and in the range of about 50-550 atmosphere. The catalyst used in the above-described run was section into 14 layers, and was found to have substantial contents of arsenic and iron as noted in below:

In 1982, Showa Electric Wire and Cable Co., Ltd. suggested that activated carbon be used to remove arsenic from naphtha. Naphtha containing 206 ppb of arsenic was mixed with powder activated carbon at a 5 volume percent dosage. Thus, the arsenic content was decreased to 10 ppb. Silverman (1985) studied a method for arsenic-removing from petroleum. In this method, arsenic was removed from hydrocarbonaceous oils by contacting the hydrocarbon with quadrolobe alumina with or without hydrogen or nitrogen at temperature of 500°F to 800°F and at pressure of 250 psi to 750 psi. The employed alumina in this study was unmodified Al_2O_3 which was prepared in the conventional manner. The particular form (eta, gamma, beta) of alumina is not critical since it served as a contacting structure rather than a catalyst. This process was run with quadrolobe alumina, as described, at various temperature and pressure. All processes were at

LHSV=0.9v/v/hr and H2/oil=1000SCF/bbl. The results showed that the efficiencies of arsenic-removing were in the range of 92.9-97.9%.

The efficiency of arsenic removal from oil is better by bringing the oil into contact with a Ni/Al_2O_3, $Ni-Mo/Al_2O_3$ or $Ni-W/Al_2O_3$ (Quang and Daniel, 1985). The mixture of oil and hydrogen was passing through a chamber comprising metal above mention at a temperature between $300^\circ C$ to $800^\circ C$. The arsenation of shale oils over nickel containing catalyst was studied with specially placed on reaching a target arsenic level of 2 ppm by Oleck et al.(1986). This process provided an improved catalyst and method for removing arsenic from shale oil. They studied the efficiency of $Cu-Mo/Al_2O_3$, $Ni/Al_2O_3-SiO_2$ and $Ni-Mo/Al_2O_3$ catalysts to find the active demetallize catalyst. They found that the dearsenation activity of $Ni-Mo/Al_2O_3$ was more active than the other catalysts. It showed that about 70% of the arsenic removed was retained on the catalyst. This is similar to the amount of nickel-containing catalysts. Thus, the retaining arsenic on catalyst was found in the form of nickel-arsenic complexes.

Child et al. (1986) suggested that the presence of nickel be the key to high dearsenation activity. The dearsenation reaction mechanism is not well understood, but the effectiveness of nickel containing catalysts in removing arsenic compounds presumably arises from the formation of stable nickel arsenide compounds such as $NiAs_2$. The results of dearsenation for nickel catalyst

and the Mobil Proprietory catalyst under identical condition was showed below:

	Arsenic Removal (Wt%)	Hydrogen Consumption (SCF/B)
Commercial Nickel Catalyst	97	200
Mobil Proprietory Catalyst	95	380

Thus, nickel containing catalyst provided superior dearsenation activity over other materials tested.

Ichikawa et al. (1988) used the catalyst to remove arsenic from heavy crude oil. The catalyst consisted of copper on alumina support and had 41 wt% of copper content. The pore volume and pore diameter was 0.141 ml/g and 40-300 A, respectively. A naphtha containing 1000 ppb of arsenic (tributylarsine or hydrogen arsenide) was contacted with this catalyst in order to decrease arsenic content. The degree of the arsenic removal was 98% comparing with initial concentration.

Literature summary

1. Arsenic in crude oil is in organometallic and inorganic forms

2. The present of arsenic in petroleum is the result of catalyst posoining. Catalyst deactivation by arsenic may result from chemical poisoning or physical blockage of the catalyst surface.

3. Three main methods are currently employed, namely thermal treatment, chemical treatment and adsorption on inorganic material. Adsortion currently the most widely used method on an industrial scale.

4. The removalof arsenic by adsorbent is prosperity in gas phases for high efficiency. On the other hand, the efficiency of arsenic removal in liquid phase is lower than gas phase. One of the factors expected for the declining efficiency of arsenic removal concerns with different forms of arsenic in gas and liquid phase.

5. An adsorbents used in arsenic removal comprise metal oxide such as Ni, Mo, Cu, Zn, Pb, or Mn or active metal supported on alumina oxide. The $NiMo/Al_2O_3$ adsorbent is preferred.

6. The operating condition for arsenic removal by adsorption in liquid phase depends on the adsorbent used. In general, the pressure range from 10-1000 psig., and the temperature interval 30^0C-200^0C.