Hydrocarbon Fuel Report

Sam White 12C
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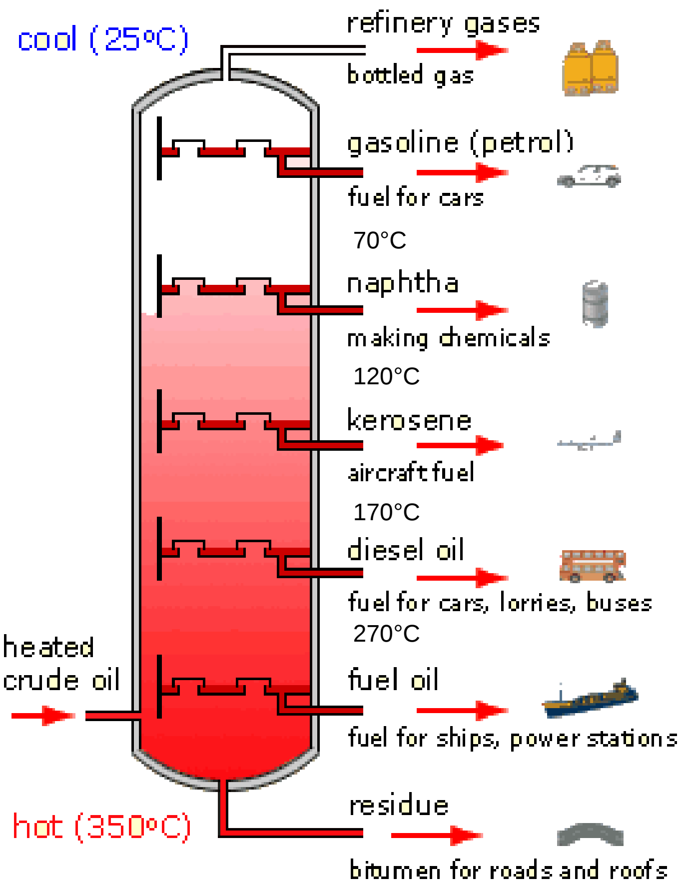
Refining

- Crude oil (also known as petroleum) is a mixture of many different hydrocarbon compounds, thus undergoes a refining process in order to transform it into different fuels such as petrol, kerosene and liquefied petroleum gas (LPG).
- The first stage of the refining process is the fractional distillation of the fuel.

Fractional Distillation

- Fractional distillation involves separating the mixture of hydrocarbons within the crude oil into separate groups of hydrocarbons with different ranges of boiling points.
- This is achieved through initially heating the crude oil to around 360°C – so its component hydrocarbons form a vapour – and then passing this vapour through a fractionating column where the temperature of the column is highest at the bottom (around 360°C) and lowest at the top (around 30°C).
- The fractionating column contains perforated metal trays at different intervals up the column where the position of the tray corresponds to a specific temperature of the fractionating column. This results in the different hydrocarbon components of the crude oil condensing on the different trays along the column as they rise and cool due to their different boiling temperatures. This therefore allows groups of hydrocarbons with similar boiling temperatures to be separated from the crude oil through collecting the hydrocarbons condensed at each tray, those which have remained as a liquid residue from the bottom of the column (bitumen) and those still in gaseous form at the top of the column (natural/refinery gas).
- The different hydrocarbon components of crude oil have different boiling temperatures due to their different carbon chain lengths where the longer the hydrocarbons carbon chain length the higher the boiling temperature (lower volatility) and the shorter the carbon chain length the lower the boiling temperature (higher volatility).
- This pattern occurs as the only intermolecular forces of attraction between the hydrocarbon molecules are induced dipole-temporary dipole forces (London dispersion forces), thus as the carbon chain length increases the greater the number of points of contact between the hydrocarbon molecules and thus the greater the strength of the London forces and also the greater the number of dipoles that can act simultaneously along the molecule length. These stronger intermolecular forces require more energy to overcome, thus the greater the boiling temperature of the hydrocarbon.
- The more volatile the fuel the greater the ease of ignition as the fuel must exist as vapour before it is combusted.

Fractionating Column



- A diagram of a fractionating column is shown to the left displaying the names of the different fractions, their uses and the approximate temperature of the fractionating column at some of the trays.
- In some refineries distillation columns are operated at less than atmospheric pressure thus lowering the temperature at which each fraction boils, thus lower temperatures can be used in the fractional distillation process. This has the advantage of reducing the possibility of unintended thermal hydrocarbon cracking.

Cracking

- Cracking is the process by which longer chain alkanes are converted into at least one alkene and shorter chain alkanes. This is needed as for some crude oil fractions (such as petrol) there is a much larger demand then there is supply of the fraction in crude oil, thus cracking is used to convert some of the longer chain alkanes, of which there is a surplus of supply, into these shorter chain hydrocarbons of which there is a deficit of supply.
- This is required as the shorter chain alkanes are more volatile and thus have a greater ease of ignition (as the hydrocarbon must be vaporised for ignition to occur) therefore making them generally better suited for use as fuels.
- There are two main types of cracking: catalytic cracking and thermal cracking.
- Thermal cracking involves heating the long chain hydrocarbons in order to thermally decompose the hydrocarbons in a pyrolysis reaction, while catalytic cracking generally involves much lower temperatures and the use of a catalyst.

Thermal Cracking

- There are different types of thermal cracking used in industry which each have different purposes.
- Visbreaking is a mild form of cracking where very high viscosity hydrocarbons are cracked in order to reduce their viscosity with negligible effects on the boiling point range of the fuel. In this process the hydrocarbons are heated at atmospheric pressure then quickly cooled using gas oil to prevent the cracking procedure from proceeding too far and significantly reducing the hydrocarbon chain length. After this process the resultant mixture is distilled to separate the added gas oil from the longer chain hydrocarbons.
- Steam cracking is another thermal cracking process often used to produce alkenes (often for polymer manufacture) from reasonably long chain hydrocarbons (generally from the naphtha fraction) involving the heating of hydrocarbons in the presence of steam. If the hydrocarbon cracked to too long then significant, undesired coke (solid carbon) deposits may result reducing the yield of the desired alkenes and reducing the reactor efficiency as the coke reduces the rate of thermal transfer from the sides of the reaction to the hydrocarbons contained within and also reducing the service life of the reactor heating element in the process.
- Coking processes are thermal cracking processes which is often used primarily with the aim of reducing the lengths to larger hydrocarbons into much smaller ones such as petrol. This process can produce large quantities of coke which is often collected and sold as a fuel. There are two main types of coking process: delayed coking and continuous coking.
- Delayed coking involves heating the hydrocarbons to high temperatures under low pressures, before the products are transferred to low pressure containers (coker drums) where it is held for around 24 hours to enable many radical propagation steps to occur in order to produce the shortest chain products possible. The products of this then undergo fractional distillation to separate the hydrocarbon products produced. Due to the large amounts of coke produced in this process the coker drums need to be cleared every few months in order to remove coke deposits that form.
- Continuous cracking involves a continuous process with temperatures higher than those used in delayed cracking provided by the transfer of thermal energy from recycled coke particles from previous cracking cycles. In this process the hydrocarbon which is being cracked is heated by these recycled coke particles in a reactor and undergoes thermal decomposition. The vapours produced are then removed from the reactor and cooled to prevent further decomposition before being separated into fractions by fraction distillation. The few remaining liquid hydrocarbons and coke are processed to remove large coke particles as a secondary product before the remaining mixture is reheated and re-introduced at the start of the process to provide the thermal energy required for further thermal decomposition.
- Although the coke produced in these thermal cracking reactions can be undesirable and may lead to inefficiencies most coke can also be utilised as a fuel (sponge coke (and small amounts of shot coke)) or as electrodes for steel production (needle coke – as it has a very low electrical resistance) thus if collected can generally be sold.

Radical Mechanism: Initiation

- The main mechanism which governs the thermal decomposition of the hydrocarbons is a radical mechanism.
- The initiation phase of the reaction generally occurs by the homolytic bond fission of one of the carbon-carbon bonds in the chain. This occurs instead of the homolytic fission of a carbon-hydrogen bond due to the greater bond dissociation energy of the carbon-hydrogen bond of 413 kJ mol^{-1} (on average) compared to the lower bond dissociation energy of 347 kJ mol^{-1} (on average).
- This bond fission is most likely to occur in a position on the carbon chain that produces the most stable radicals thus the energy required for the bond fission will be lowest in these positions. These differences in radical stability are due to the hyperconjugative effects of the σ bonds in alkyl groups on orbitals containing radicals through their effect of delocalising the electron deficiency of the radial thus the greater the number of alkyl groups directly bonded to the carbon atom with radical the greater the delocalisation of the negative deficiency and thus the more stable the radical.
- Naturally if the carbon chain contains a π bond the conjugative effects of this due to the resonance structures introduced will further delocalise the electron deficiency, thus leading to even more stable radicals. This thus leads to a weakening of the carbon-hydrogen bonds attached to the β-position carbon to the π bond due to the extra stability of forming a allyl radical, thus making carbon-hydrogen bond fission much more likely to occur instead of carbon-carbon bond fission.

Propagation

- After the initiation phase of the reaction many different propagation reactions may occur such as hydrogen atom abstraction, addition, radical decomposition and radical isomerization reactions.
- Hydrogen atom abstraction reactions may occur between radicals and other hydrocarbons and involve the transfer of a hydrogen atom from the non-radical species to the radical species.
- This process follows the same guidelines as those established on the initiation page where the most likely reaction to occur is that which results in the most stable radical being formed, thus for example for the reaction between a ethyl radical and propane the most likely reaction is the abstraction of one of the hydrogens on propane’s second carbon atom thus forming a secondary propyl radical (stabilised through the hyperconjugation of the two neighbouring methyl groups) and ethane as opposed to the abstraction of a hydrogen atom on the first carbon atom which would result in a primary propyl radical forming which would only be stabilised by a single methyl group.
- Radical isomerization may also occur (mostly in longer chain radicals) where groups of atoms are moved to different locations along the radical through the formation of an intermediate ring. This could result in the relocation of the unpaired radical electron from a less stable position to a more stable position (e.g. from a primary to secondary location).
- Radical decomposition occurs by the homolytic fission of one of the carbon-carbon bond in the chain to produce another, shorter, radical and an alkene. The most common decomposition that occurs is the fission of the β-position to α-position carbon bond in straight chained alkyl radicals, thus this process effectively shifts the unpaired electron to the β-position carbon.
- In alkanes where the unpaired electron is located on a branch from the α-position carbon the bond fission may generate two different sets of products dependent on the bond which undergoes the fission with alkanes and radicals of different structures being produced in each case. Similarly in allyl radicals if the carbon in the β-position to the unpaired electron is involved in a double bond the carbon-hydrogen bonds on the carbon radical will be weakened, due to the great stability of forming a conjugated alkene with two double bonds, thus there may be an equal chance of the formation of hydrogen radicals and a conjugated alkene compared to the chance of forming a shorter allyl radical and an alkene.

Termination

- In the thermal cracking of hydrocarbons termination normally occurs through the reaction of two radicals to form a non-radical species in an addition reaction, however termination may also occur if the radicals collide with the side of reactor.
- When two radicals collide in a termination reaction they can either combine to form a single species (recombination) or form an alkene and a alkane (disproportionation).
- The reaction mechanism may also start to cease if the hydrocarbon mixture is rapidly cooled – such as is the case in visbreaking and in the product extraction processes of other thermal cracking methods – as then this will largely reduce the likelihood that radical decomposition and other propagation processes will occur as the energy supplied to the system will be lower than the activation energy for these reactions.

Molecular Reactions

- Secondary products can be produced such as polycyclic aromatic hydrocarbons after the primary products form in the thermal cracking process.
- One mechanism through which coke can form is through the dehydrogenation of polycyclic aromatic hydrocarbons which can be produced through secondary reactions.
- One method by which aromatic products can form is through a Diels-Alder reaction which a conjugated diene and alkene (acting as a dienophile) react together forming a cyclical hydrocarbon. This reaction occurs due to the greater stabilisation associated with the formation of more σ bonds as opposed to the relatively less stable π bonds in the reactants. The cyclical compound formed may then undergo dehydrogenation to form an aromatic substance.

Catalytic Cracking

- Catalytic cracking involves reasonably high temperatures and moderately low pressures and yields a reasonably high yields of branched an cyclic alkanes.
- There are three main types of catalytic cracking processes: fluid catalytic cracking (FCC), moving-bed catalytic cracking and Thermofor catalytic cracking (TCC).
- Fluid catalytic cracking is the most common cracking process in industry and involves small solid catalyst particles (such as zeolites) being introduced to hot crude oil and its vapours in a reactor. This mixture hence behaves like a fluid due to the suspension of the catalyst within the oil. The catalyst in this mixture promotes the cracking of the crude oil into smaller fractions before fractional distillation is carried out to separate the products produced. As the catalyst remains solid it can easily be differentiated from the reaction products and is reintroduced at the start of the cracking process to facilitate the further cracking of hydrocarbons.
- During this catalytic cracking coke is produced which will reduce the effectiveness of the catalyst as it coats the catalysts active sites. Catalyst particles which have been exposed to large amounts of coke are regenerated in a regenerator where the coke is burnt off, thus allowing the catalyst to operate at optimum efficiency and also elevating the heat within the reactor when the catalyst is reintroduced.
- The zeolite catalysts used possess a crystalline structure containing many micro-pores which hydrocarbons enter through to access the catalyst active sites (hence why coating the catalyst in coke reduces its efficiency). At the active sites within the crystal the cracking process is facilitated by the catalyst adsorbing the hydrocarbon molecules and causing the hydrocarbon to undergo a dehydrogenation process leading to the formation of carbocations which act as intermediate species in the cracking process.
- The carbocations formed from alkanes then tend to isomerize into more stable forms (as governed by hyperconjugation and the inductive effects of the neighbouring alkyl groups) and may then undergo bond fission of the carbon-carbon bond in the β-position (relative to the carbocation) resulting in the formation of an alkene and shorter alkane carbocation (which will subsequently stabilise through isomerization process). This β-scission is most favourable if the carbocation is in a second or third degree position. Other possible reactions that may occur involve the carbocation undergoing further dehydrogenation (to form an alkene), it undergoing hydrogenation (to form an alkane) or reacting with an alkene in a alkylation reaction. This cracking process is generally faster when the initial species is an alkene as they have a larger tendency to form the initial carbocation.

Reforming

- Reforming is a process used to improve the octane rating (a measure of the knocking effects of a fuel based on its similarity to the behaviour of a specific mixture of heptane and 2,2,4-trimethylpentane (iso-octane) where behaviour like a 100% iso-octane mixture is rated as 100 and behaviour like a 100% heptane mixture is rated as 0) of fuels and thus reduce their tendency for pre-ignition in combustion engines resulting in engine knocking.
- Reforming processes increase the octane number of fuels through the formation of branched isomers of the original fuels which the form more stable radicals within the combustion process due to the hyperconjugative/inductive stabilisation effects of the increased number of alkyl groups connected to the electron deficient carbon atom containing the radical. These more stable radicals are then less likely to decompose as quickly as the non-stabilised radicals hence the combustion reaction is more controlled, hence the higher octane number attributed to branched hydrocarbon species.
- An example of a reforming process is through the use of a bifunctional catalyst with platinum impregnated onto the surface of aluminium oxide. In this process the alkane is adsorbed onto the catalyst and undergoes dehydrogenation to form an alkene and subsequently react with a hydrogen ion on the surface of the catalyst in order to form a carbocation. Isomerization reactions nay then occur stabilising the carbocations formed into secondary and tertiary ions before forming an alkene through a further dehydrogenation process and being released from the catalyst until it is re-adsorbed onto another active catalyst site where it is hydrogenated to form an alkane. This process is similar to that within the catalytic cracking process, however the temperatures used during this are not high enough to result in β-scission of the alkane, but are high enough to just allow the isomerization reactions to occur. Cyclical alkanes and aromatic species may also be formed during this process, however if the hydrocarbons involved in this process have sulphur impurities then these impurities may be adsorbed more favourably than the hydrocarbons and could lead to the formation of coke.

Environmental Safeguarding Techniques Used

- Although crude oil comprises mainly of hydrocarbons it also contains smaller amounts of other elements such as sulphur and nitrogen.
- Sufficiently high sulphur content in crude oil may damage equipment and deactivate catalysts used in the refining process as well as produce sulphur oxides when the fuel is burnt which – when released into the atmosphere – may react with water vapour to form sulphuric and sulphurous acids which contribute to acid rain which can result in the death of aquatic life forms, damage historic monuments (especially those made of limestone due to its basic nature) and damage the waxy cuticle on the leaves of plant life.
- As such within the refining process sulphur compounds are removed from crude oil through various desuphurisation processes, such as the use of catalysts and high temperature mechanisms to form hydrogen sulphide gas which is then subsequently treated.
- The presence of nitrogen compounds in fuel may lead to the formation of nitrogen oxides during the combustion process. If these are released into the atmosphere these can also react with water vapour in order to form nitric acid which will also contribute to acid rain formation. Nitrogen oxides also play a role in ozone depletion and are involved in reactions that destroy ozone and subsequently regenerate nitrogen oxides e.g. $NO + O_3$ –> $NO_2 + O_2$ and $NO_2 + O$ –> $NO + O_2$. This is unfortunate as ozone forms a layer around the earth which acts to help shield the earth's surface from ionising ultraviolet radiation. In addition to this they can also play a role in the eutrophication of some aquatic systems leading to the death of some highly oxygen dependent species and a reduction in biodiversity.
- Unlike sulphurous compounds nitrogen compounds are difficult to remove from fuels during the refining process as they are combined with organic matter, thus the principle methods involved in reducing the release nitrogen oxides into the atmosphere are methods involving the treatment of exhaust gasses to reduce the nitrogen oxides into nitrogen and water (e.g. through the use of catalytic converters) or through carrying out combustion in fuel rich conditions (with low oxygen concentrations) initially to reduce the likelihood of any produced nitrogen compounds forming nitrogen oxides, before further air is added after the initial combustion to allow complete combustion of the fuel to occur.
- If combustion occur in an environment with an insufficient supply of oxygen then incomplete combustion may occur producing solid carbon particles (such as soot) and carbon monoxide as not enough oxygen is available to oxidise these products into carbon dioxide. The carbon particulates may lead to the onset of lung diseases such as bronchitis if inhaled and may also act as a carcinogen. The carbon monoxide produced is also toxic as when inhaled it forms a more stable complex with the haemoglobin in the blood than oxygen thus while oxygen and carbon dioxide are able to mutually replace each other in the complexes they form with the haemoglobin this is cannot occur with carbon monoxide due to this greater complex stability. This can thus lead to death due to the insufficient transfer of oxygen and carbon dioxide around the body.
- In some combustion engines it is ensured that excess air is available within the engine thus increasing the likelihood that complete combustion will occur. This fuel-air mixture within the engine is controlled by the carburettor within the engine which may change the mixture depending on the products of the combustion that are being detected. Catalytic converters are also used to encourage the oxidation of the solid carbon and carbon monoxide molecules. Also in some thermal oxidisers very high temperatures are used as this will increase the rate at which the oxidation occurs.

Combustion

- The combustion which these fuels eventually experience after the refining process occurs via a radical mechanism which can generally take place via two different pathways: a high temperature low pressure pathway and a lower temperature higher pressure pathway, although the basis of both pathways lies within the reaction classes of the higher temperature mechanism.
- In the following slides the higher temperature pathway has been focussed upon.

High Temperature Mechanism Reaction Classes

- The high temperature reaction mechanism is comprised of nine reaction classes these are:

1). Unimolecular fuel decomposition

2). Alkane hydrogen atom abstraction

3). Alkyl radical decomposition

4). Alkyl radical reactions with oxygen producing an alkene and hydroperoxyl (HO_2) radical

5). Alkyl radical isomerization

6). Alkene abstraction reactions by hydroxyl (OH), hydrogen (H), oxygen (O), and methyl (CH_3) radicals

7). Addition of radicals to alkenes

8). Alkenyl radical decomposition

9). Alkene decomposition

Likely Mechanism Route

- The combustion reaction is usually started for the hydrocarbon fuel through the attack of the fuel with hydroperoxyl (HO_2), Hydrogen (H), Oxygen (O), or hydroxyl (OH) radicals resulting in the formation of an alkyl radical and either hydrogen peroxide, hydrogen, a hydroxyl radical or water respective to the attacking radical. The initial initiation step occurs through the homolytic fission of a carbon-carbon or carbon-hydrogen bond in a single hydrocarbon molecule.
- After this initial attack and the formation of the alkyl radical in the high temperature reaction mechanism the radical is most likely to undergo decomposition forming another, shorter radical species and alkene until the size of the radical reduces such that it forms an ethyl or methyl radical as until this time reactions with molecular oxygen, oxygen radicals or alkyl recombination is unlikely due to the high temperature making radical decomposition by β-scission the most favourable reaction pathway.
- After the formation of the methyl radical it is likely that an reaction with an oxygen radical will occur to form formaldehyde which will subsequently undergo multiple hydrogen atom abstractions to form carbon monoxide which will then be oxidised into carbon dioxide.
- If the temperature is too low or the pressure to great to facilitate the favourable β-scission of the alkyl radicals then it is likely that the alkyl radical will undergo an addition reaction with molecular oxygen and start down the low temperature reaction pathway with the formation of an alkylperoxy radical before undergoing an isomerization to form a hydroperoxylalkyl radical which may then decompose into a variety of products depending on further conditions.

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