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# Shale Oil & Gas: A study on refining

A Technology Landscape

Aug-13



# **Contents**

| 1. Introduction   | 1  |
|---|----|
| 2. Background   | 2  |
| 3. Market Research                                      | 2  |
| 3.1 Major players in shale oil and gas refining         | 3  |
| 3.2 Mergers and acquisitions (M&A) in shale oil and gas | 4  |
| 4. Technical Overview                                   | 6  |
| 4.1 Refining of shale oil                               | 7  |
| 4.1.1 Distillation                                      | 7  |
| 4.1.2 Pyrolysis   | 8  |
| 4.1.3 Cracking  | 9  |
| 4.1.4 Filtering   | 10 |
| 4.1.5 Chemical Treatment                                | 10 |
| 4.1.6 Reheating   | 12 |
| 5. Application and products of shale oil                | 12 |
| 5.2.1 Cement Preparation                                | 12 |
| 5.2.2 Raw fuel Preparation                              | 12 |
| 5.2.3 Hydrogen Production                               | 13 |
| 5.2.4 Power generation                                  | 13 |
| 5.2.4 Other products generation                         | 13 |
| 6. Patent Trend Analysis                                | 13 |
| 6.1 Geographical Distribution                           | 13 |
| 6.2 Filing Trends                                       | 14 |
| 6.3 Top Assignees                                       | 15 |
| 7. Technical Analysis                                   | 16 |
| 7.1 Refining vs. Usage of shale oil                     | 16 |
| 7.2 Refining of shale oil                               | 17 |
| 7.2.1 Distillation of shale oil                         | 18 |
| 7.2.2 Chemical Treatment of shale oil                   | 19 |
| 7.2.3 Pyrolysis of shale oil                            | 19 |

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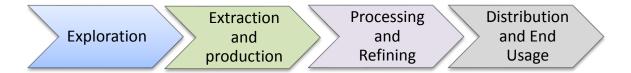
| 7.2.4 Filter for shale oil                                  | 20 |
|---|----|
| 7.2.5 Cracking for shale oil                                | 21 |
| 7.3 Usage of shale oil                                      | 21 |
| 8. Conclusion   | 22 |
| About us  | 24 |
|   |    |
|   |    |
|   |    |
| List of figures   |    |
| Figure 1: Taxonomy for refining the shale oil and its usage | 6  |
| Figure 2: Geographical Distribution of Patents              | 14 |
| Figure 3: Filing Trend of Patents                           | 15 |
| Figure 4: Assignee chart                                    | 16 |
| Figure 5: Categories of patents based on refining and usage | 16 |
| Figure 6: Subcategories of refining                         | 17 |
| Figure 7: Subcategories of distillation                     | 18 |
| Figure 8: Subcategories of chemical treatment               | 19 |
| Figure 9: Subcategories of pyrolysis                        | 20 |
| Figure 10: Subcategories of filtering                       | 20 |
| Figure 11: Subcategories of cracking                        | 21 |
| Figure 12: Subcategories of usage                           | 22 |
| List of Tables  |    |
| Table 1: Major companies in shale oil and gas refining      | Δ  |
| Table 2: List of mergers and acquisitions                   |    |
| Table 2: List of mergers and acquisitions                   |    |



## 1. Introduction

Shale oil (light tight oil) is rapidly emerging as a significant, and relatively low cost, unconventional energy resource. There is potential for shale oil production to spread globally over the next couple of decades. If this does happen, it would revolutionize global energy markets, providing long term energy security at lower cost for many countries. A recent report from US energy information administration says that shale based resources could potentially increase the world's total oil supplies by 11 percent. It is predicted, in a report of PWC, that global shale oil production has the potential to reach up to 14 million barrels of oil per day by 2035; this amounts to 12% of the world's total oil supply.<sup>1</sup>

The below value chain is associated with shale oil and gas. While in some countries exploration and use of shale oil and gas energy is still in conceptualization phase, in others like USA and China, shale oil and gas is already in use commercially. They have successfully exploited the entire value chain and developed fitting technologies and a market. China is found to be filing patents aggressively in the domain of refining shale oil and gas. In our study we have focused on exploring 'processing and refining' of shale oil and gas.



For years, oil and gas companies have known liquid oil is locked up in shale formations. Using advanced drilling techniques companies are now able to recover the liquid oil from great depths. Oil and gas companies drill deep below the surface and then turn their drill bits to create horizontal wells. Once completed, they blast water, sand and chemicals at a high pressure into the wells which opens up fissures in shale formations and allows oil and gas to be pumped to the surface. Shale rocks contain a waxy substance, kerogen which when intensely heated liquefies to produce a precursor to crude oil. The shale crude oil so obtained is further refined before sending it to commercial markets.

This article attempts to analyze the patent landscape of shale oil and gas refining to bring out the evolution of this technology and market insights.

<sup>&</sup>lt;sup>1</sup> Shale oil: the next energy revolution [<u>Link</u>]



# 2. Background

Shale oil is one of the first sources of mineral oil used by humans. It was used to light the streets of Modena, Italy at the turn of the 17th century. The British Crown granted a patent in 1694 to three persons who had found a way to extract and make large quantities of pitch, tar, and oil out of a sort of stone. The discovery of crude oil in the Middle East during 19th mid-century brought most of these industries to a halt, although Estonia and Northeast China maintained their extraction industries early into the 21st century. Due to development of new technologies like horizontal drilling and fracking, and the increasing difficulties related to cost and availability of crude oil, the focus is now shifting back to shale oil and gas extraction as a viable source of energy. One of the recent instances was in Texas in the 1980s, where George Mitchell combined horizontal drilling with hydraulic fracturing to extract natural gas safely and economically<sup>2</sup>.

The rise of shale gas and oil has been one of the major developments in the world of energy, which will have a lasting impact for years to come. While shale production efforts have been around for decades in the United States, recent studies and discoveries in other parts of the world have changed the global energy landscape. Shale oil and gas is considered as the next "light bulb innovation" in the field of energy



Shale oil and gas is termed as the next "computer innovation" in the field of energy that has the potential to become an alternative of conventional energy sources.

## 3. Market Research

Global shale oil production could potentially reach up to 14 million barrels of oil per day by 2035; which would amount to nearly 12% of the world's total oil supply. It also estimates that this increase could reduce oil prices in 2035 by around 25%-40% (\$83-\$100/barrel in real terms) relative to the current baseline EIA projection of \$133/barrel in 2035 (assuming low levels of shale oil production). In turn, this could increase the level of global GDP in 2035 by around 2.3%-3.7% (This equates to around \$1.7-\$2.7 trillion at today's global GDP values). Large net importers of oil and gas like India and Japan are will benefit the most benefited from this<sup>3</sup>.

Price of shale oil and gas plays an important role in exploration and production as it provides incentive for exploration, production and extraction. Shale oil and gas is an expensive sector due to the low probability



<sup>&</sup>lt;sup>2</sup> Shale oil and gas [<u>Link</u>]

<sup>&</sup>lt;sup>3</sup> Shale oil: the next energy revolution [Link]



of finding profitable wells. According to David Hughes, geoscientist and fellow at the Post Carbon Institute, 72000 shale wells must be drilled annually in USA for production to remain constant at the cost of \$42 billion dollars. The production from shale wells can drop by 95% in three years<sup>4</sup>. Add to that exploration costs of new viable wells and it is a substantial cost. If the prices of oil and gas fall below a certain threshold, companies will be discouraged to continue investing in the industry. This scenario could lead to Wall Street initiated mergers and acquisitions to take advantage of scale and market coverage.

Companies involved in the extraction and production of shale oil and gas are not the only companies benefitting from this industry. Manufacturers of steel piping, builders of rail tank cars, and express package deliverers are some of the businesses who are impacted positively.



The extraction of shale oil and gas is capital intensive process and requires the technical edge in "fracking" and "horizontal drilling".

# 3.1 Major players in shale oil and gas refining

Filing for patents is an essential part of a company's strategy. Companies working on refining shale oil and gas technologies have increased their patenting activity in recent years to strengthen their position in the market. Also, companies are aggressively acquiring patents via mergers and acquisitions. The landscape analysis for shale oil and gas refining show the leading companies in this field.

| Sr.No. | Company Name  | Revenues for the fiscal year 2012-13 (\$ Billion) | Shale oil and gas business News  | Number<br>of<br>Patents |
|--------|---|---|--|-------------------------|
| 1      | Chemical Petroleum<br>and Chemical<br>Corporation (CNPC) or<br>Sinopec limited,<br>Beijing, China | 450   | Recently launched its shale oil and gas project and it expects to churn out 6.5 billion cubic meters of shale gas for domestic use by 2015 | 7                       |



<sup>&</sup>lt;sup>4</sup> Faster drilling, Diminishing Returns in Shale Plays Nationwide? [<u>Link</u>]



| 2 | Chengda Hongsheng<br>Energy Co., Ltd.,<br>Huadian city in Jilin<br>Province of China | 1.878 (natural gas<br>and pipeline<br>business achieved<br>operating revenue<br>in 2010) | Plans a total investment of 5.7 billion yuan (about \$1 billion) for the oil shale comprehensive development project  Annual production of oil shale (shale rock) will be 6,000,000 tons and shale oil 500,000 tons. The heating and electric power for the whole city will be provided. | 7 |
|---|--|--|--|---|
| 3 | Fushun Mining Group, Fushun in Liaoning Province of China                            | NA   | One of the world's largest shale oil producers  Consists of about 30 smaller companies   | 5 |
| 4 | VKG Oil AS, Kohtla-<br>Järve, Estonia  | NA   | 250,000 tons of shale oil per year,<br>with over 2 million tons of the so-<br>called "brown gold" being<br>processed   | 2 |
| 5 | Exxon Mobil<br>Corporation, Irving,<br>Texas, USA                                    | 467  | One of the patents is describes chemical treatment while another is about pyrolysis  | 2 |

Table 1: Major companies in shale oil and gas refining

# 3.2 Mergers and acquisitions (M&A) in shale oil and gas

The M&A activity in shale oil and gas has increased manifolds in last couple of years. Below are some mergers and acquisitions and purchase of assets by various companies in this industry:



A number of Chinese companies like CNPC, Chengda Hongsheng Energy Co., Ltd. are filing aggressively in the field of refining of shale oil and gas.



| Sr.<br>No. | Acquiring<br>Company                             | Acquisition/Joint Venture/Seller of Assets           | Region of Exploration/Production   | Year |
|------------|--|--|--|------|
| 1          | Schlumberger<br>Limited⁵                         | Smith International                                  | -  | 2010 |
| 2          | Chinese National<br>Petroleum Corp. <sup>6</sup> | Royal Dutch Shell Inc.                               | For the construction of a liquid natural gas plant in Canada to develop and produce shale gas              | 2012 |
| 3          | Total S.A. <sup>7</sup>                          | Chesapeake Energy<br>Corp. (CHK) and<br>EnerVest Ltd | Acquired a \$2.32 billion holding in Ohio's Utica shale region. Interested in shale exploration in Britain | 2012 |
| 4          | Schlumberger<br>Limited <sup>8</sup>             | Forrest Oil Corp.                                    | To develop eagle ford (also called the Eagle Ford shale) in South Texas in United States                   | 2013 |
| 5          | EXCO Resources                                   | Chesapeake Energy<br>Corporation                     | Eagle ford   | 2013 |
| 6          | Sanchez Energy's<br>SN Marquis                   | ZaZa Energy<br>Corporation <sup>10</sup>             | Eagle ford   | 2013 |
| 7          | Rosneft <sup>11</sup>                            | Statoil ASA  | Shale oil in the Samara region in the southeastern part of European Russia                                 | 2013 |

Table 2: List of mergers and acquisitions



Mergers and Acquisitions activity in last 5 years shows that corporate world is serious about presenting shale oil and gas as alternative form of energy that can last long.



<sup>&</sup>lt;sup>5</sup>Schlumberger finalizes \$11B merger with Smith International [Link]

<sup>&</sup>lt;sup>6</sup>Royal Dutch Shell, CNPC Ink First Chinese Shale Gas Production-Sharing Deal [<u>Link</u>]

<sup>&</sup>lt;sup>7</sup>Chesapeake Energy Corp. creates a joint venture with Total S.A. to drill Ohio Utica shale [Link]

<sup>&</sup>lt;sup>8</sup> Schlumberger [<u>Link</u>]

<sup>&</sup>lt;sup>9</sup>Exco Resources Inc. deal with Chesapeake Energy Corporation [Link]

<sup>&</sup>lt;sup>10</sup>ZaZa Energy [Link]

<sup>&</sup>lt;sup>11</sup>Statoil and Rosneft move forward with exploration cooperation [<u>Link</u>]



#### 4. Technical Overview

There are several techniques by which shale oil is refined and the way shale is used as a raw material. The method of refining the shale oil varies depending upon the end products and their usage. Figure 1 show taxonomy followed during the entire study:

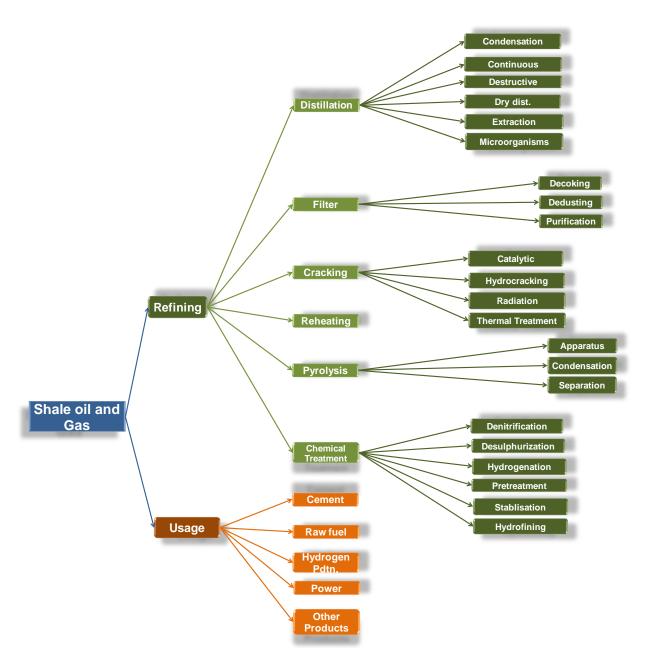


Figure 1: Taxonomy for refining the shale oil and its usage



# 4.1 Refining of shale oil

Shale oil once extracted is processed and refined into more useful products. This process of refining shale oil may be done by distillation, cracking, pyrolysis, chemical treatment or filtering. Reheating helps in using the input energy more efficiently.

#### 4.1.1 Distillation

Distillation is the most common processing technique in oil refineries. Shale oil is distilled into various fractions of different boiling ranges, each of which are then processed further if required. The process of shale oil distillation is done by gasification of oil at high temperatures. The distilled oil is collected and is sent for further processing and refining. Following are the different types of distillation.

#### 4.1.1.1 Continuous Distillation

Continuous distillation is a type of distillation where kerogen is continuously fed into the distillation chamber. The separated fractions of kerogen which are the components of shale oil are removed continuously. Continuous distillation has a minimum of two output fractions of raw oil. The first one is the residual solid and the second one is the gaseous fractionates. The gaseous output is collected and condensed into different fractions. The solid residual can be further processed. A continuous production of synthesis gas through direct gasification contained in oil shale is disclosed in WO2012126596A1.

#### 4.1.1.2 Destructive Distillation

Destructive distillation is the chemical process involving the decomposition of shale oil by heating to a high temperature in the absence of air or in the presence of limited amounts of oxygen or other reagents, catalysts or solvents. Patents <a href="Months of CN102776010A">CN102776010A</a> and <a href="Months of CN101649214A">CN101649214A</a> discloses the process of destructive distillation of shale oil.

#### 4.1.1.3 Dry Distillation

Dry distillation is the process of heating solid shale rock to produce gaseous products. The products are condensed and collected. This method usually requires higher temperatures than classical distillation. In the patents <u>US8312927B2</u> and <u>US20080290000A1</u> the process of shale oil dry distillation by gasification of input oil using high temperature and collecting the required fractions, and sending for processing further are discussed.



#### 4.1.1.4 Extraction

Extraction is the separation process where a substance is separated from a mixture. It may be liquid-liquid extraction or solid phase extraction. Extraction of Hydrocarbons from the shale oil is disclosed in US2010173806A1.



Patent <u>US20120100588A1</u> discusses the distillation of shale oil using micro-organisms. A method for recovering hydrocarbons from oil shale and other carbonaceous materials has the steps of preparing a biomedium of microorganisms, water, and nutrients; providing shale laden with oil; treating oil shale with the biomedium; mechanically agitating the treated oil shale and biomedium approximately twelve hours to form a liquid suspension; and separating the components of the liquid suspension to yield a hydrocarbon mixture.

#### 4.1.1.5 Condensation

In condensation the physical state of fractionates of distilled shale oil is changed from gaseous phase into liquid phase. In <u>US8312927B2</u> and <u>US8312928B2</u> patents, a detail explanation of condensation step performed to recover shale-oil products from the gas is given.

#### 4.1.1.6 Micro-organisms

Micro-organisms are also used for distillation. Kerogen is mixed with bio-medium which contains microbes to form a suspension which is kept undisturbed for a time. These immiscible layers are then separated carefully.

#### 4.1.2 Pyrolysis

Pyrolysis is a thermochemical process where organic rich material is decomposed at elevated temperatures in the absence of oxygen (or any halogen). It is coined from the Greek-derived elements pyro ("fire") and lysis ("separating").

#### **4.1.2.1 Decoking**

Decoking is also known as decarbonizing, is a process where carbon matter is removed from the feedstock by refining the shale oil. Patents <a href="Mailto:CN100545236C">CN100545236C</a> and <a href="CN201046951Y">CN201046951Y</a> disclose the process of decoking the shale oil to carbon vapor and collected.



#### 4.1.2.2 Condensation

In condensation the physical state of fractionates of kerogen is changed from gaseous phase into liquid phase. Patents <u>US8336621B2</u> and <u>US5388534A</u> discloses that pyrolizing the low grade solid fuel to produce combustible gases which are collected separately by condensation.

#### **4.1.2.3** *Separation*

In our study separation is defined as a process where kerogen is distinct into two or more fractionates, where one of fractionate is enriched into one or more of the oil's constituents. In some cases separation process may fully divide the shale oil into its pure constituents. Patents <u>US7718038B2</u> and <u>US5013428A</u> mention the collection of separated fractionates based on the viscosity after the shale feedstock is pyrolized.

#### 4.1.3 Cracking

Cracking is the process where heavy hydrocarbons such as shale oil are broken down into simpler molecules such as light hydrocarbons due to carbon-carbon bonds breakage in the precursors. The rate of cracking and the end products are strongly dependent on the temperature and presence of catalysts.

#### 4.1.3.1 Catalytic Cracking

The catalytic cracking process occurs in the presence of acid catalysts where long carbon chain is heterolytic (asymmetric) breaks into a carbo-cation and the very unstable hydride anion gets rearranged to form stable chains. Patents <a href="US5344553A">US5344553A</a> and <a href="CN102453546A">CN102453546A</a> mention the cracking of shale oil in to simple hydrocarbons using different catalyst like one Group VIA or Group VIII metal and hydrogen gas respectively.

#### 4.1.3.2 Hydrocracking

Hydrocracking is a catalytic cracking process assisted by the presence of an elevated partial pressure of hydrogen gas. Similar to the hydro-treater the function of hydrogen is the purification of the hydrocarbon stream from sulfur and nitrogen hetero-atoms. Hydrocracking is disclosed in patents <u>US20040238406A1</u> and <u>WO2008061304A1</u>. The patents mention the extraction of simpler hydrocarbons from shale oil.

#### 4.1.3.3 Radiation Cracking

Cracking of shale oil using radiation like microwave, resonance frequency waves etc. come under this type of cracking. In patent application <u>US20100096295A1</u> shale oil is exposed to microwave radiation for a sufficient time to obtain fractionates. Patent application <u>AU2010221564A1</u> discuss about heating of shale oil by using RF radiation for duration.



#### 4.1.3.4 Thermal Cracking

Thermal cracking of shale oil is the one of the oldest technique which occurs at high pressure of about 7,000 KPa where hydrogen-rich products like kerogen are condense by losing hydrogen to forms simple alkanes. <a href="Mailto:CN102877823A">CN102877823A</a> mentions the cracking method adopting a blasting principle for improving a gas output for shale gas.

#### 4.1.4 Filtering

Filtering is the simple process used for the separation of solids from fluids (liquids or gases). This is done by passing the mixture through a medium which allows only passage of fluids. The process of filtering is done where removing micro-dust adhered on solid material surface for retorting is required or likewise in other processes.

#### 4.1.4.1 De-dusting

De-dusting is the simple process where micro dust particles are removed from the surface of shale oil crush for further refining. During refining it can occur in many places, like when removing micro-dust adhered on solid material surface for distillation. The similar type of process is disclosed in <a href="Mailto:CN202081062U">CN202081062U</a> and <a href="EP2583753A1">EP2583753A1</a> where dust obtained from the vapor gas mixture is de-dusted.

#### 4.1.4.2 Purification

Purification is the physical separation of a shale oil fractionates of interest from extracted shale oil. Patents like <a href="Mailto:CN100553736C">CN100553736C</a> and <a href="CN1002824823A">CN102824823A</a> discloses the process of purification of shale oil into pure fractionates.

#### 4.1.5 Chemical Treatment

Nearly all fractionates are chemically treated before going for packaging. The method of treatment depends of the type of fractionate and the intended use of the finished fractionate. These treatments remove impurities such as sulfur and nitrogen compounds, which damage the machinery and pollute the air when burned.

#### 4.1.5.1 De-nitrification

Hydro-treating is a process of treating kerogen in the presence of catalysts hydrogen which results in denitrification (removal of nitrogen compounds) and conversion of olefins to paraffin. Patent <a href="Moleonization-continuous conversion of olefins">CN101967392B</a> discloses a method for de-nitrification refining of shale oil at a specific conditions.





#### 4.1.5.2 De-sulfurization

Hydro-treating is a process of treating kerogen in the presence of catalysts hydrogen which results in desulfurization, (removal of sulfur) and conversion of olefins to paraffin. Patent <u>US7981276B2</u> mentions a process for removing sulfur from sulfur-containing hydrocarbon streams utilizing a multi-ring aromatic hydrocarbon complex containing an alkali metal ion from the shale oil.

#### 4.1.5.3 De-metallization

The process of removing traces of metal from the kerogen has been subjected to a metal-based catalysis reaction in the patent <a href="Mailto:CN1066284A">CN1066284A</a> process for removing and transformation of mineral material from oil shale is discussed.

#### 4.1.5.4 Hydrofining

Hydrofining is a chemical process involved in the shale oil refining in which hydrocarbons of feedstock are hydrogenated and desulfurized or denitrified catalytically to obtain a pure product. <a href="CN102465015A">CN102465015A</a> and <a href="CN102311788A">CN102311788A</a> are the patents which relates to this process of hydrogenation of shale oil in the presence of catalyst.

#### 4.1.5.5 Hydrogenation

Hydrogenation means to treat the compounds with hydrogen. It is a chemical reaction between molecular hydrogen (H2) and shale oil usually in the presence of a catalyst. <a href="Molecular-No.101067089B">CN101067089B</a> mentions the hydrogenation of shale oil to obtain separated light product; dry gas, liquefied gas, gasoline, diesel oil and catalytic heavy oil.

#### 4.1.5.6 Pretreatment

Before refining, shale oil passes through a chemical pretreatment process. <u>US5277796A</u> relates to pretreating oil shale prior to retorting with organic acid which reduces mineral carbonates content, particularly calcite and dolomite, of the oil shale and increases subsequent retorting yield.

#### 4.1.5.7 Stabilizing

Stabilization is a process where chemicals are added to shale oil to improve the stability of the end product and the yield rate. <a href="Months:CN101323789A">CN101323789A</a> and <a href="CN101323789A">CN1048277C</a> disclose the process of stabilizing the shale oil before refining.



#### 4.1.6 Reheating

Reheating is the one of the refining technique of shale oil where either hot air gas is re-circulated into the feed stock, or input shale oil is moved to the chamber for further extraction of desired product. Patent <a href="Moving International CN101270292B">CN101270292B</a> discloses a method where a tail gas is circulated into different temperature region repeatedly and patent <a href="CN101619221A">CN101619221A</a> discloses a method where continuous circulating the carrier material is described.

# 5. Application and products of shale oil

Shale can be used as a fuel for thermal power plants for generating electricity. Here it burns like coal to drive steam turbines. Shale oil serves best to produce middle-distillates such as kerosene, jet fuel, and diesel fuel. In addition to its use as a fuel, shale oil may also serve in the production of specialty carbon fibers, adsorbent carbons, carbon black, phenols, resins, glues, tanning agents, mastic, road bitumen, cement, bricks, construction and decorative blocks, soil-additives, fertilizers, rock-wool insulation, glass, and pharmaceutical products. However shale oil usage for these items remains in experimental stage.

Products of shale oil refining, whether waste residues or refined fractionates, are both useful. Its concentration of high-boiling point compounds is suited for the production of middle distillates, and additional cracking can create the lighter hydrocarbons used as raw fuels. The shale oil directly derived may not be as useful as the end products because it may contain higher concentrations of olefins, oxygen, and nitrogen than conventional crude oil.

#### **5.2.1 Cement Preparation**

After refining of shale oil, the left residue of shale oil waste is utilized in the production of cement clinkers. Such processes are mentioned in the patents <a href="Mailto:CN102491701A">CN102491701A</a> and <a href="CN102433144A">CN102433144A</a>.

#### 5.2.2 Raw fuel Preparation



#### 5.2.3 Hydrogen Production

Production of gases like Hydrogen, carbon monoxide, carbon dioxide and other gases from shale oil raw material is common. Patents <u>US7070758B2</u> and <u>US20120309070A1</u> relate to the hydrogen gas production from shale oil.

#### **5.2.4 Power generation**

Different process of generating the electricity at industrial level from the shale oil are described in the patents of <u>US20090050532A1</u> and <u>US8043592B2</u>. Patent US8043592 describes how the silicon dioxide starting materials are combined with a primary energy provider containing hydrocarbon to start a first reaction. During this first reaction, the silicon dioxide containing starting material is heated and crystalline silicon is produced. Then, the crystalline silicon is used in a second reaction which runs exothermically (i.e., releases heat).

#### 5.2.4 Other products generation

Both shale oil and its residual wastes are used for the production of other products at industrial level. Patent <u>US6258300B1</u> describes production of active carbon fiber, and patent <u>CN101020765A</u> describes production of natural rubber filler. Patent <u>CN102465036A</u> describes a process of producing propylene by oil shale.

# 6. Patent Trend Analysis

The patent filing in technologies related to refining of shale oil and gas is growing rapidly. This is primarily because it presents an alternative to present conventional sources of energy, and also because we now have technologies that can extract and refine shale oil and gas economically and safely. Post 2006, companies all over the world have started filing patents aggressively. USA and China are leading the race. The prospect of shale oil and gas drastically reducing national crude oil imports makes utilization of this technology an attractive opportunity. Thus the corresponding patent filing trend is expected to grow further.

# **6.1 Geographical Distribution**

**Figure 2** shows the geographical distribution of the patents in shale oil and gas refining. An analysis of the patents reveals that maximum number of patents (about 23%), were filed in China, about 20% patents were filed in the US followed by Europe, Canada and Australia with 10%, 7% and 7% patent filings respectively. The reason for China's dominance is that this energy source has exploited since long and it was never abandoned with the onset of crude oil.



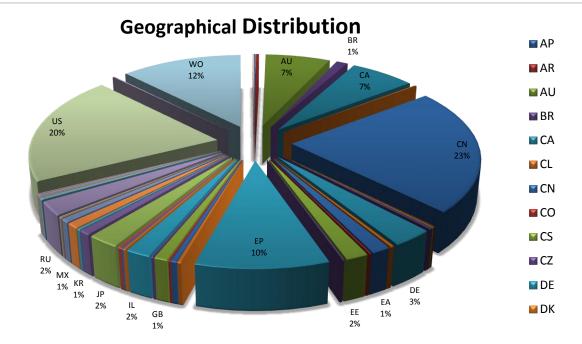


Figure 2: Geographical Distribution of Patents

As indicated the number of filings in China and USA, since 1990, is 164 and 144 respectively. Australia, Canada and Europe have 47, 47 and 70 patent filings respectively. Other countries which have shown considerable interest in shale oil and gas technology are Russia, Japan, Israel, Estonia, Brazil, Mexico, Great Britain, South Korea, and New Zealand.

# **6.2 Filing Trends**

The increase in the filing trend is clearly visible in the **Figure 3**. 80% of the total applications were filed 2005 onwards. The uptrend in filing from 2005 in shale oil and gas can be attributed to the increase in focus towards the alternative energy sources and development of new technologies to refine shale oil and gas. Chinese companies have drastically increased patent filings. Sinopec and Shenyang Chengda Hongsheng Energy have filed about 7 patents each and Fushun Mining Group has filed 5 patents. University of North Eastern China has 6 patents of its own as well.



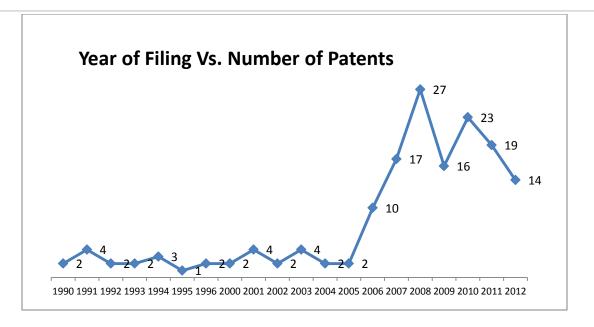


Figure 3: Filing Trend of Patents



The filing of patents for refining of shale oil and gas after 2005 has gone straight up. This tremendous increase in filing could be attributed to the aggressive filing by Chinese

# 6.3 Top Assignees

**Figure 4** shows the number of patents filed by various organizations. 20 patents have been filed by individual inventors. Chemical petroleum and Chemical Corporation (CNPC) or Sinopec limited have filed 7 patents of which 5 are filed in chemical treatment category, 4 in hydrofining sub category, and 1 in hydrogenation. 7 patents have been filed by Chengdu Hong Sheng energy Co., Ltd. 5 out of these patents are in distillation category and 1 in pyrolysis and 1 in filtering. There are 6 patents filed by University of North Eastern China. ExxonMobil has 4 patents while VKG oil and Total Corporation have filed 2 patents each.

It is evident from the figure below that Chinese corporation and Universities are the leading assignees in patents related to shale oil and gas refining.



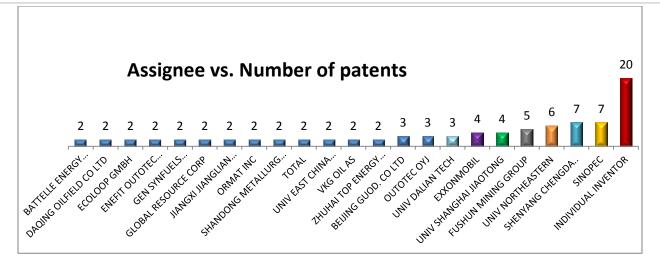


Figure 4: Assignee chart

# 7. Technical Analysis

Once the novelty was defined the patents were categorized. The categories here are all exclusive and do not overlap. The analysis revealed that patents in the portfolio (158 patents) have refining and usage of raw or residue shale oil as the broad two categories. Refining of shale oil involves multiple steps and the process can be made faster, effective and less costly by altering or improving some steps.

# 7.1 Refining vs. Usage of shale oil

As shown in **Figure 5**, including refining and usage of shale oil there are 158 patents in all. About 122 patents i.e. about 77% of the patents are for refining and the remaining 36 patents describe use of raw shale oil material or shale oil residue.

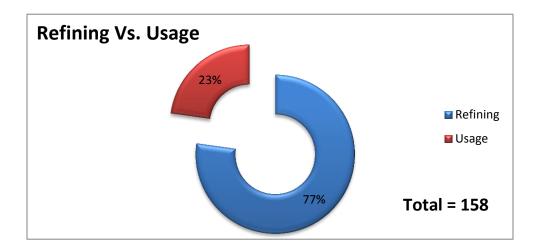


Figure 5: Categories of patents based on refining and usage



# 7.2 Refining of shale oil

**Figure 6** shows classification of patents based on the sub categories of refining of shale oil. About 55 out of 122 patents discuss about distillation process. 22 and 19 patents are about pyrolysis and chemical treatment respectively. 10 are about pyrolysis, 8 relate to cracking, and 8 patents describe cracking and reheating methods. Distillation is the most important primary step in refining processes. Distillation, pyrolysis and cracking attribute about 67% of the total patents in refining category. Filtering and chemical treatment attribute about 22% of the total refining patents whereas reheating is about 7% only. Reheating can make the entire process more efficient. From this analysis it can be concluded that the area remains relatively unexplored.

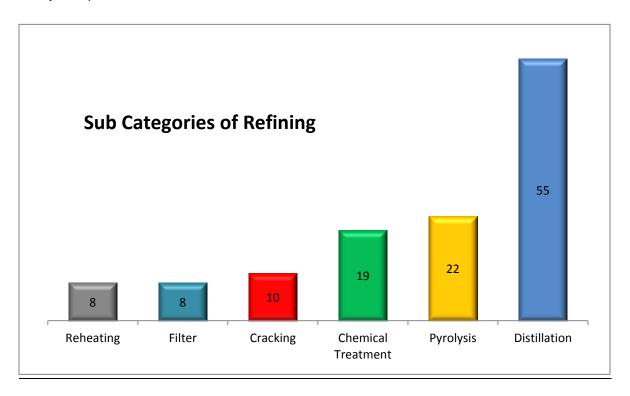


Figure 6: Subcategories of refining



#### 7.2.1 Distillation of shale oil

In distillation sub category 38 out of 55 patents are in dry distillation. Patents such as <u>US8312927B2</u> describe the process of shale oil dry distillation done by gasification of input shale crude oil, using high temperature to collect the required fractions. 8 out of 57 patents relate to condensation, such as <u>US8312928B2</u> which describes in detail the condensation step performed to recover shale crude-oil products from the gas is given. 6 out of 55 patents relate to destructive distillation. Patent <u>CN101649214A</u> discloses continued distillation, extraction and micro-organisms.

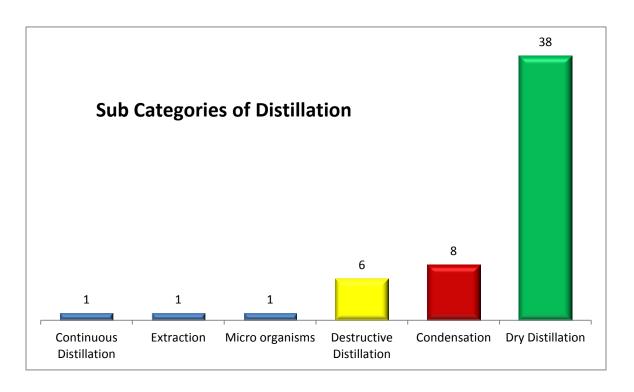


Figure 7: Subcategories of distillation



#### 7.2.2 Chemical Treatment of shale oil

**Figure 8** shows detailed information of patents related to shale oil's chemical treatment. 4 out of 19 patents each are related to the stabilization, hydrofining and hydrogenation, 2 each describe pretreatment, desulfurization and de-metallization, and 1 patent relates to de-nitrification of shale oil. <a href="https://doi.org/10.2016/j.cn/cn1048277C">CN1048277C</a> discloses the process of stabilizing the crude shale oil before refining it. <a href="https://doi.org/10.2016/j.cn/cn1048277C">CN102465015A</a> and <a href="https://doi.org/10.2016/j.cn/cn1048277C">CN102465015A</a> are patents which relate to the process of hydrogenation of crude shale oil in the presence of catalyst and <a href="https://doi.org/10.2016/j.cn/cn1048277C">CN101967392B</a> discloses a method for de-nitrification refining of shale oil at a specific conditions.

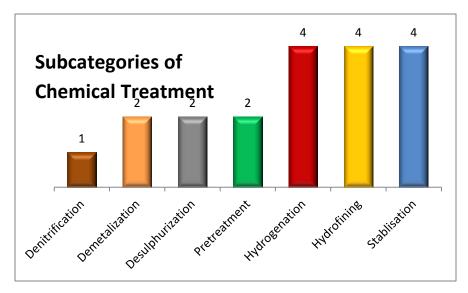


Figure 8: Subcategories of chemical treatment

### 7.2.3 Pyrolysis of shale oil

**Figure 9** shows classification of patents describing pyrolysis technologies according to 3 subcategories. 11 out of 17 patents relate to separation, 9 patents describe about the condensation and 3 patents are about decoking of shale oil. <u>US5388534A</u> describes pyrolizing the low grade solid fuel to produce combustible gases which are collected separately by condensation. <u>US5013428A</u> patents explains the collection of separated fractionates based on the viscosity after the crude feedstock is pyrolized, and <u>CN201046951Y</u> discloses the process of decoking the crude shale oil to carbon vapor.



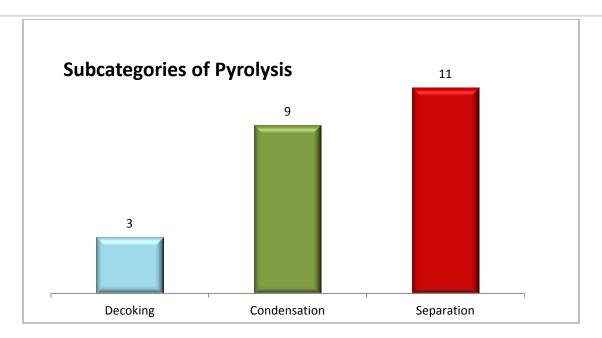


Figure 9: Subcategories of pyrolysis

#### 7.2.4 Filter for shale oil

The classification of patents describing filtration of shale oil is shown in **Figure 10**. 5 out of 13 patents are about purification and 2 patents are related to de-dusting of shale oil. <u>EP2583753A1</u> discloses de-dusting where the dust is obtained from the vapor gas mixture and patents <u>CN100553736C</u> and <u>CN102824823A</u> disclose the process of purification of crude shale oil into pure fractionates.

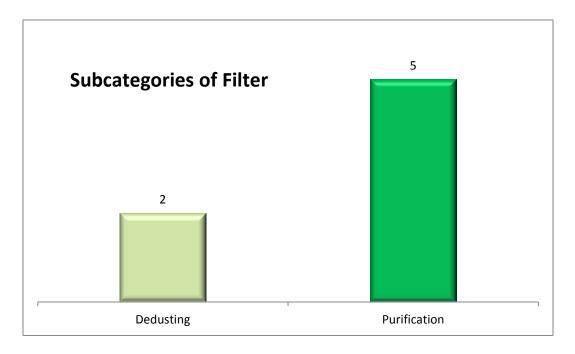


Figure 10: Subcategories of filtering



#### 7.2.5 Cracking for shale oil

The categorization of patents involving cracking of shale oil is shown in **Figure 11**. 3 out of 10 patents each are about hydrocracking and radiation, 2 out of 10 patents each relate to catalytic and thermal treatment of shale oil. In <u>US20100096295A1</u> a method is described that involves exposure of crude shale oil to microwave radiation for sufficient time leads to obtaining fractionates. <u>US5344553A</u> and <u>CN102453546A</u> are about the cracking of crude shale oil in to simple hydrocarbons using different catalysts, like one Group VIA or Group VIII metal and hydrogen gas respectively. <u>CN102877823A</u> describes a cracking method adopting a blasting principle for improving a gas output for shale gas.

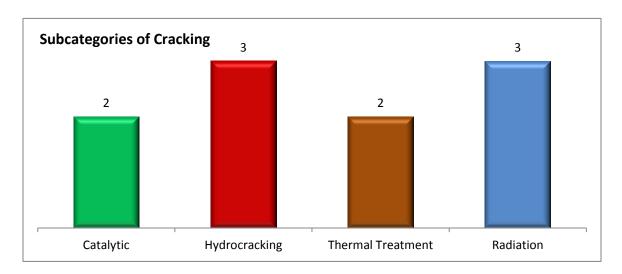


Figure 11: Subcategories of cracking

# 7.3 Usage of shale oil

In our study, usage of shale oil and gas is defined as the use of raw shale or the usage of waste residue remaining after distillation. **Figure 12** shows classification of patents based on the subcategories of usage of shale oil. About 14 out of 36 patents discuss about usage as raw fuel, 8 out of 36 patents discuss about production of various products, 7 out of 36 patents about power generation, 5 out of 36 patents discloses cement preparation and 2 patents relates to hydrogen production. After refining of shale oil, the left residue of shale oil waste is used in the production of cement clinkers which are discussed in the patents <u>CN102491701A</u> and <u>CN102433144A</u>. Raw fuel like marine fuel, jet engine fuel, modified carbon black, etc. are produced using the shale oil residue which is a waste obtained after refining the crude shale oil. These are described in the patents of <u>WO2005028596A1</u>, <u>CN101254922A</u>, <u>US6101959A</u>. Different process of generating the electricity in the industrial level from the shale oil are described in patents <u>US20090050532A1</u> and <u>US8043592B2</u>, while <u>US6258300B1</u> says about production of active carbon fiber and <u>CN101020765A</u> discusses production of natural rubber filler. <u>CN102465036A</u> and <u>CN102173750A</u> describe production of simple olefins from shale oil.



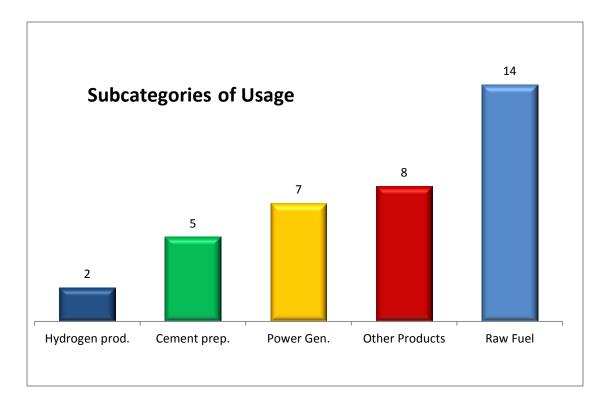


Figure 12: Subcategories of usage

# 8. Conclusion

Preliminary studies suggest that there are more than 650 shale formations worldwide, in 142 basins. This amounts to 458 TCM of shale gas of which 40% is estimated to be economically recoverable. Geographically, the US and CIS countries are estimated to account for nearly 60% of available shale gas resource worldwide. Europe however, accounts for only 7% of global shale reserves, though these estimates are subjected to change with every new exploration<sup>12</sup>. A US Department of Energy report in 2011 estimated that the largest reserves of shale gas in Europe are in Poland. The authors of the report calculate that Poland has reserves of about 22.45 trillion cubic meters of shale gas, of which 5.30 trillion cubic meters is immediately available for extracting<sup>13</sup>. Chevron is at various stages of exploration in a number of countries, including Argentina, Canada, China, Lithuania, Poland, Romania and Ukraine<sup>14</sup>. On

<sup>&</sup>lt;sup>12</sup> Comparison of shale gas in USE and CEE [Link]

<sup>&</sup>lt;sup>13</sup> Shale gas by country [Link]

<sup>&</sup>lt;sup>14</sup> Natural gas from shale [<u>Link</u>]



the other hand Total S.A. is exploring the United States, Argentina, China and Australia in the hopes of finding shale oil and gas<sup>15</sup>.

We are on the cusp of an oil and gas revolution. The rocks containing shale oil and gas could power the world for the coming decades. Unfortunately only 2.5 percent of the countries in the world are able to produce and use shale oil and gas. Those countries who are sleeping through this phase of energy revolution might find themselves strategically outmatched in a few years when it comes to exploiting this resource. Countries using oil & gas exports as a foreign policy to dictate terms and condition may find themselves losing their might and the same may happen to crude oil giants unless they factor shale oil and gas into their plans. This is indeed a great opportunity, especially due to rising crude oil prices, to explore a new viable option to serve our energy needs in the near future.

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 $<sup>^{15}</sup>$  After USA and Argentina Total is consolidating position worldwide. [Link]



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