

Improvisation of Coke Quality by Co-Carbonization of Vacuum Residue and Bio Oil: A Batch Process

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Abstract: Effects of feed properties during co-carbonization of vacuum residue (VR) and bio oil feed mixed in different proportions in a batch reactor at temperature range of 480°C-490°C and at atmospheric pressure on coke lumps produced after reaction was studied and proposed based on experimental results obtained. Detailed experimental study was done on co-carbonization process of bio-oil and vacuum residue mixed in different proportions in an experimental setup capable of producing solid coke comparable to that produced in commercial delayed coker which helps to study effects of parameters like temperature and pressure on product properties. Product yield and specifications of products and feed were recorded and studied in terms of thermogravimetric analysis. Coke produced was analyzed as compared to Anode grade coke, for its spongy appearance and catalogued based on its properties when compared with anode grade coke. Addition of bio oil to vacuum residue up to 1:1 indeed ameliorate the hardness of coke and reduce the VCM content of coke, transforming it to better quality sponge coke and can be used as anode grade coke. Coke yield was improved by increasing micro carbon residue (MCR) weight percentage. Additionally, asphaltene content of feed directly contribute to solid product yield and gas yield reinforce the anisotropy of coke formed that govern the coke quality. Bio-oil enhance the gas yield till 1/1 mixture required to improve the coke quality.

Keywords: Bio-oil, Vacuum residue, batch, coke.

I. INTRODUCTION

Co-carbonization of various feedstocks has been studied by many authors and its effect on quantity, quality and formation mechanism of coke had been reported [1]-[5]. Moreover, the effect of various properties of feedstock and process variables on above mentioned properties have been reported in detail to optimize the process of delayed coking and to produce better quality coke.

The present authors have studied the co-carbonization of Vacuum Residue (VR) and Bio-Oil at 480°C-490°C, for it has not been studied yet and both feedstocks are available in abundance. Coke formed in a batch reactor is comparable to coke recovered in a delayed coker [3],[7]. Therefore, parameters like temperature and pressure can be experimentally optimized at laboratory level later to be used in commercial delayed coker.

Revised Manuscript Received on October 15, 2019

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The present study highlights the quantity and quality of coke formed by feedstocks formed by mixing both feeds in various proportions.

Furthermore, effect of various components of feed on coke formed had been studied and a comparison is made with Anode grade coke properties to check coke grade.

II. EXPERIMENTAL

A. Process Diagram

As shown in fig. 1 co-carbonization of various feedstocks was carried out in 1 Litre batch reactor which was purged with nitrogen for maintaining inert environment. Reactor was completely insulated from outside with glass wool jacket to prevent any heat loss to the surrounding. Both spiral and double pipe heat exchangers were used to condense the heated vapours and lower its temperature from 485°C to room temperature (25°C). Water was used as cooling agent at 4°C to condense the vapours. The condensed vapours were collected in a Büchner flask whereas components which are in gaseous state at room temperature escapes to atmosphere after passing through 0.5 litre gas flowmeter which is used to record volume of gas evolved.

B. Process Description

Total five feed samples of weight 200 g each were obtained by mixing both feedstocks at 120°C. Some data regarding feedstock is given in Table I obtained by SARA analysis, sulphur analysis, Micro carbon residue (MCR) analysis. Metals like nickel (Ni) and vanadium (V) are measured in parts per million (ppm). Feed samples produced were in VR to Bio-Oil ratio of Pure VR, 03:01, 01:01, 01:03 and Pure Bio-Oil. Additionally, 2 g of distilled water is added to feed to prevent coking and maintain minimum vapor velocity in tubes. [7],[8],[11]. Samples were carbonized in a batch reactor at 485°C and 1 atm [10]. Reaction Temperature is controlled by PID controller. A ramp function of 4°C / min was input to reach desired temperature, then temperature was kept constant until the completion of reaction. Nitrogen is purged initially to maintain inert environment inside the reactor. Reaction was considered to start once temperature reaches 485°C and was considered completed when gas flowmeter stops. Vapours evolved were condensed in a couple of heat exchangers and condensed liquid product was collected in a trapper. Remaining gases were disposed to vent after passing through gas flowmeter.

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Recovered products were weighed and analysed, coke formed in the reactor was removed mechanically and analysed under Thermogravimetric analysis (TGA) for hardness and types of components and trapped hydrocarbons [9]. Similarly, liquid and gaseous products were examined for various

properties like sulphur, micro carbon residue (MCR), viscosity, gas chromatography, saturates, aromatics, resins and asphaltenes (SARA) [12].

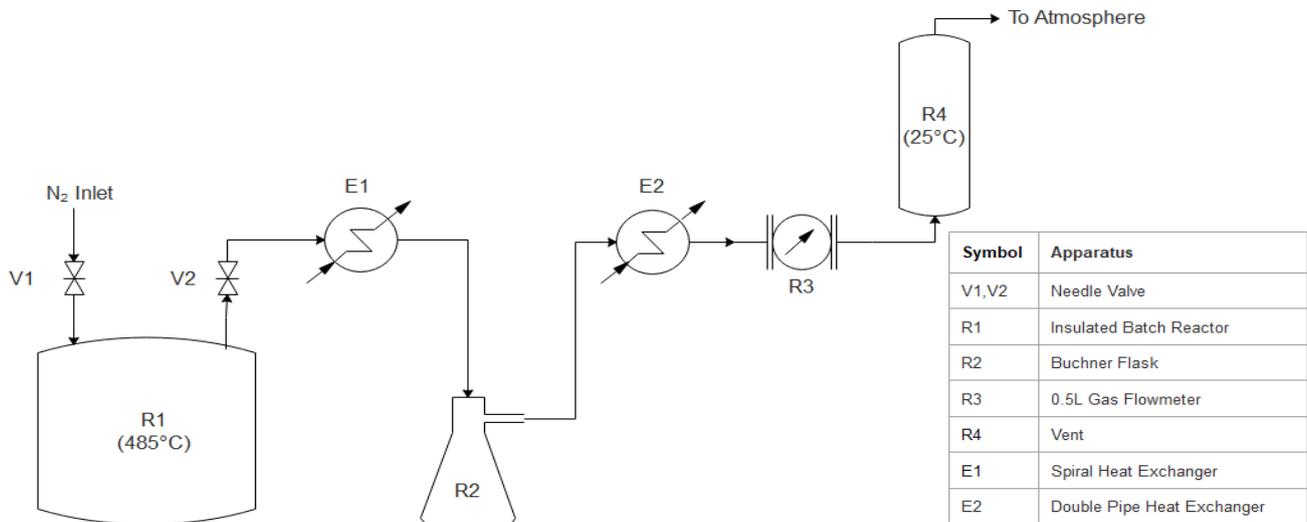


Figure 1 Process diagram of co-carbonization of feed

• Determination of Sulphur:

For evaluating Sulphur concentration in the feeds and liquid products of the batch runs, oxford lab-x3500 sulphur analyser was used which is based on spectroscopy i.e. x-rays are used to excite the electrons in the sample, spectrum is formed when electrons returned to initial stage and this spectrum is used to determine the sulphur concentration of the sample. This method is based on ASTM4294. Samples are installed in special type of cups with Poly-M base. Cups were installed in instrument and weight percentage of sulphur was displayed digitally

• Determination of Micro Carbon Residue (MCR):

ACR-M3 is a tester to be used for the determination of the amount of carbon residue formed after evaporation

Table I: Characteristics of vacuum residue feedstock

Components		Concentration
Saturates	Weight percentage(wt%)	33.28
Aromatics		17.87
Resins		34.82
Asphaltenes		14.03
MCR		26.19
Sulphur		6.15
Ni	ppm	36
V		135

and pyrolysis of petroleum material under certain conditions and is intended to provide some indication of the relative coke forming tendency of such materials. Standard method ASTM D4530 is employed in this instrument to measure MCR. A weighed quantity of sample is placed in a glass vial and heated to 500°C under an inert (nitrogen) atmosphere in a controlled manner for a specific time. Small vials are installed with sample in them and machine is run under controlled flow of nitrogen gas to meet inert conditions. After result vials are weighed and calculation are done for micro carbon residue.

• Thermo Gravimetric Analysis:

Delayed coking sample runs are examined under both nitrogen and air environment for liquid and coke respectively and temperature range is set to 30°C to 900°C with a ramp function of 4°C rise per minute. The obtained data from TGA experiment is then finally divided into 4 section comprising of Naphtha (<150°C), Atmospheric gas oil (AGO) (150°C-350°C), Vacuum gas oil (VGO) (350°C-565°C) and Vacuum residue (VR) (>565°C). This classification is used for liquid products from bath runs. On the other hand, coke is exposed air in the TGA and undergoes combustion. Prior to examining coke, it is completely disposed of any liquid absorbed in it by dipping coke in toluene for 24-48 hrs. and later dried completely. Resulting data gives the hardness of the coke and volatile trapped hydrocarbons.

III. RESULTS AND DISCUSSION

A. Yield

Product yield is given in table II. Table summarizes the percentage yield of solid coke, liquid and gaseous products formed during carbonization of

Table II: Weight percentage yield of products formed.

Feed	Pure VR	VR: Bio Oil (3:1)	VR: Bio Oil (1:1)	VR: Bio Oil (1:3)	Pure Bio Oil
Solid	38.73	33.65	24.23	20.33	14.83
Liquid	51.29	56.77	63.94	72.29	79.06
Gas	5.81	6.80	9.73	3.52	3.36

Table III: Weight percentage of MCR in feed and coke yield.

Feed	Pure VR	VR: Bio Oil (3:1)	VR: Bio Oil (1:1)	VR: Bio Oil (1:3)	Pure Bio Oil
MCR (wt%)	26.19	23.29	14.15	12.65	4
Solid Coke (wt %)	38.73	33.65	24.23	20.33	14.83

Table IV: Time for coking completion at 485°C

Feed	Pure VR	(3:1)	(1:1)	(1:3)	Pure Bio Oil
Time (hr.)	0.75-1	2-2.5	4-4.5	3.0-3.5	2.5-3

pure VR, Bio-Oil and their respective mixtures mentioned above. It has been found that with increasing bio oil concentration coke yield decreases but liquid product yield increases simultaneously. Whereas the gaseous products show peak structure having maximum gas yield in 01:01 mixture feed sample. Based on appearance coke is sponge coke based on its highly porous and sponge like appearance [11]. The coke yield increase is directly in relation with Micro carbon residue (MCR) of the feed as mentioned in table III. Coke yield is directly proportional to the MCR of the feed [6].

B. Carbonization Progress:

Completion period required by reaction for different feedstocks are summarized in table IV. It has been noted that bio oil is more stable than VR as it required 2.5- 3 hr. whereas later required 45 min – 1 hr. at 485°C. Contrary to trend it has been noted that time for reaction completion increases till 1:1 (VR: Bio-oil) then decreases.

C. TGA of Coke:

Thermogravimetric analysis of coke was performed in air where its combustion had been taken place from 30°C to 900°C, recording the derivative weight loss percentage per minute and plot is shown in fig. 2. Prior to TGA analysis coke is dried at 100°C to dry it off moisture content. A trough was observed in 100-200°C range which signifies the weight loss due to evaporation of volatile carbon matter (VCM) and

entrapped hydrocarbons. Pure Bio oil’s coke has been recorded with deepest trough signifying the large evaporation of hydrocarbons and volatile carbon matter. On the other hand, this dip in 01:01 and 01:03 sample coke TGA analysis are smallest depicting its low VCM content and better-quality coke. Fig. 3 clearly signifies the quality of 01:01 coke is superior to the other and it can be used as sponge coke in aluminium industry after checking its other specifications [9]. Dip observed in high temperature range is mainly due to burning of coke forming CO₂ and signifies the hardness of coke. Similar to above results 01:01 as shown in Figure 3 coke has lowest dip which depicts the hardness of coke is relatively highest among five as here is no significant loss recorded. On the other hand, pure bio oil coke is softest among five samples. Hardness of coke is mainly due to conversion of amorphous structure to crystalline structure on heating therefore increasing its anisotropy [13]. Addition of bio-oil is bolstering the hardness by forming more anisotropic coke and diminishing the VCM content up to 01:01, After that both of the properties record fall and produces poor quality coke. Gas yield during carbonization leads to good flow texture of axial arrangement and anisotropic structure formation, enhancing the quality of coke formed [1]. Gas yield was maximum recorded in 1:1 feed, ultimately quality of coke produced was best among all coke produced from batch runs.

IV. CONCLUSION

Detailed experimental method is followed to study the effects of different proportions of feed mixture on the specifications of coke produced.

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Various properties of solid coke were studied to determine the quality of coke formed and compared with anode grade coke. Based on appearance coke formed from all feeds were sponge coke [11]. Solid product formed by 01:01 feed was hardest coke formed. Increase in bio-oil concentration up to 50% bolsters the hardness of coke. Increment in Vacuum residue concentration enhances the MCR content and

asphaltene content which directly contribute to coke yield. Gas yield contribute to improve the anisotropy of the coke form crystalline coke. Moreover, in this study attempts were made to find best concentration of mixture to form best quality of coke.

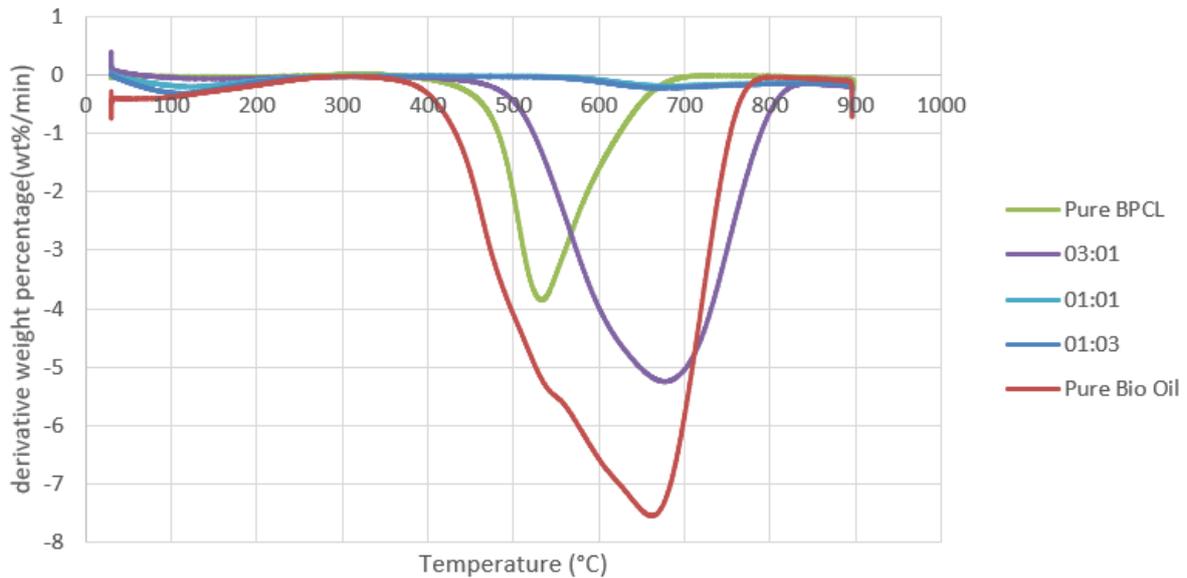


Figure 2: Derivative weight (%. min⁻¹) vs temperature (°C) of all five feedstock.

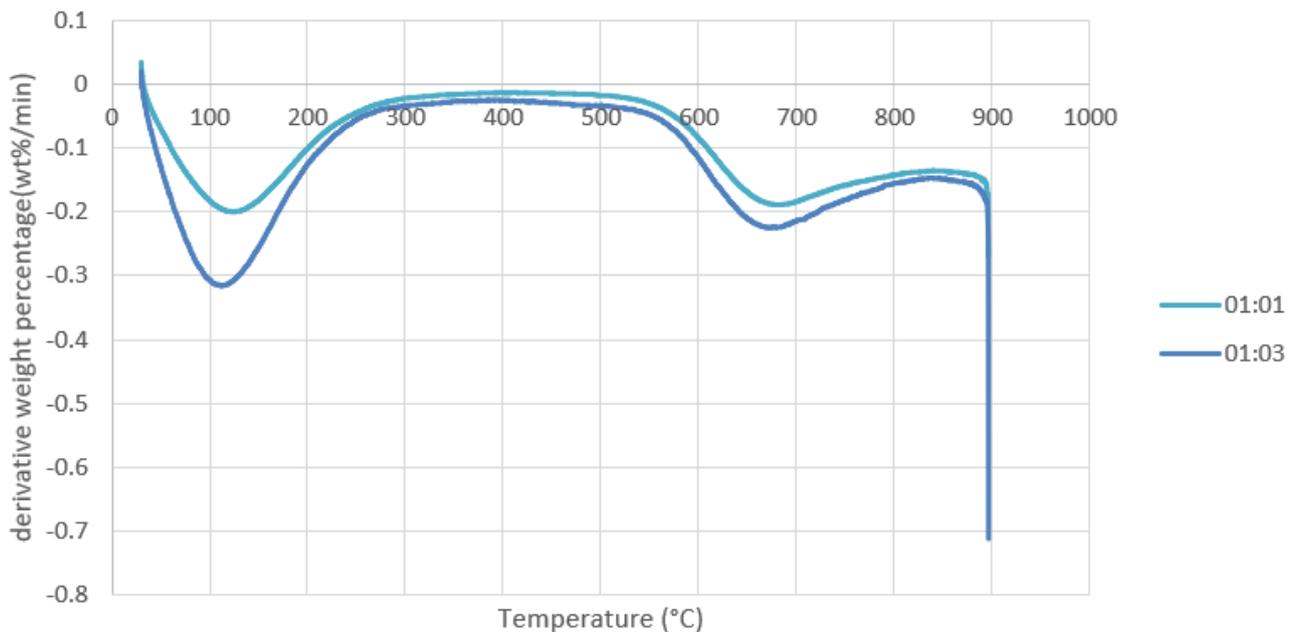


Figure 3: Derivative weight (%. min⁻¹) vs temperature (°C) of 01:01 and 01:03 feedstock

REFERENCES

1. Mochida, I., and Korai, Y., "Mechanism of Cocarbonization Of Petroleum Vacuum Residue And A FCC-Decant Oil", Carbon, vol. 27, pp. 359-365, 1989.
2. Nesumi, Y., Todo, Y., and Oyama, T., "Carbonization in The Tube Bomb Leading to Needle Coke: II. Mechanism of Cocarbonization Of A Petroleum Vacuum Residue And A FCC-Decant Oil", Carbon, vol. 27, pp. 367-373, 1989.
3. Mochida, I., Korai, Y. and Fujitsu, H., "Evaluation of Several Petroleum Residues as The Needle Coke Feedstock Using A Tube Bomb", Carbon, vol. 25, pp. 259-264, 1987.
4. Mochida, I., Oyama, T., and Korai, Y., "Formation Scheme of Needle Coke from FCC-Decant Oil", Carbon, vol. 26, pp. 49-55, 1988.
5. Stadelhofer, J.W., Marrett, R., and Gemmeket, W., "The manufacture of high-value carbon from coal-tar pitch", Fuel, vol. 60, pp 877-882, 1981
6. Sawarkar, A.N., Pandit, A.B., Samant, S.D., and Joshi, J.B., "Petroleum Residue Upgrading Via Delayed Coking: A Review", The Canadian Journal of Chemical Engineering, vol. 85, pp. 5, February 2007.
7. Speight, J.G., The Chemistry and Technology of Petroleum, 4th Ed., Ch. 3, pp. 410, and 501, CRC Press, Florida, 2006.

8. Fahim, M.A., Al-Sahhaf, T.A., and Elkilani, A.S., Fundamentals of Petroleum Refining, 1st Ed., pp. 133,136, and 137, Elsevier, Amsterdam, 2010.
9. Prasad, R., Petroleum Refining Technology, 1st Ed., pp. 207, Khanna Publishers, New Delhi, 2008.
10. Chaudhary, U.R., Fundamentals of Petroleum and Petrochemical Engineering, 1st Ed., pp. 81, CRC Press, Florida, 2010.
11. Meyers, R.A., Handbook of Petroleum Refining Processes, 3rd Ed., 12.53, and 12.69, McGraw-Hill Education, 2003.
12. Tianguang Fan, et al., "Evaluating Crude Oils by SARA Analysis" Society of Petroleum Engineers, Proceeding of SPE/DOE Improved Oil Recovery Symposium, pp. 14, April 2002, Tulsa, Oklahoma
13. Clark, J.G. (2008). Delayed coking of south African petroleum residues for the production of anode grade coke and automotive fuels, pp. 38

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Prabhsimran Singh did his bachelors of engineering in Chemical Engineering at Thapar Institute of Engineering and Technology, Patiala, India. He did his 6-week training under quality analysis department of United Breweries at Ludhiana, India. He did his Industrial training done from Indian Institute of Petroleum, Dehradun, India in Delayed coking. He is working as a Graduate Engineer Trainee in production of insoluble Sulphur from soluble Sulphur at Oriental Carbon and Chemical Limited, Dharuhera, India. His future research interests are related to petroleum and polymerization sector of chemical engineering and vision is to bring about disruptive changes in above mentioned sectors.



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