Properties of Modified Bitumen Obtained from Natural Bitumen by Adding Pyrolysis Fuel Oil

H. Kazemi Esfeh, B. Ghanavati, and T. GhaleGolabi

Abstract—**There are large mines of natural bitumen around the world and low price make it a good opportunity for increasing of industrial usage of this material. This paper studies the possibility of producing new material in oxide bitumen properties range from combination of natural bitumen and pyrolysis fuel oil. To achieve this goal first used some experiments to determine the physical properties of raw materials and then after combining more natural bitumen and pyrolysis fuel oil in different samples some test including penetration, softening point and ductility test have been done and results have been compare to ASTM and BS standard. Ultimately seen this combination can produce bitumen with R115/15 and R95/25 grade.**

Index Terms—**Asphalt, Bitumen, Gilsonite, P.F.O.**

I. Introduction

Natural bitumen is usually byproduct that have petroleum base and they produced from underground storages stones or they will rise up on its surface by ground layers. If bitumen rises on the ground surface it can constitute bituminous springs and if stay inside the ground and closed its force path it will be solidified and oxidized and extremely it will make a solid and hard substance that called mineral bitumen. Gilsonite is mineral bitumen, black and brittle, which is easily crushed into powder [1].

Natural bitumen is used in different industries such as petroleum production road making, found, making covers and making colors but natural bitumen directly is not used in this industry and usually it is added to the base material in the form of additive material. This combination can have different purposes like improvement of physical or chemical properties produce production with more variety or produce production with less final cost. In the petroleum derivation process that can mentioned to the shale stabilization. These additives have not any kind of effects on swelling pressure. Also, their significant bulk size prevents them from entering shales and effectively blocking pore throats. Therefore, filtrate invasion and mud pressure penetration will proceed unretarded [2]. Also in foundry industry seacoal and gilsonite are used by the as carbonaceous additives in green molding sands [3]. We can mention to making ink as color among natural bitumen applications. A typical ink formulation is spread pigment in the phenolic resins. Lithographic ink is made of 10% pigments, 10% resins and a balance of ahydrophobic solvent such as hydrocarbon oil. This hydro carbonic oil is high viscosity oil having a boiling range of 310–550 8C. Common resins used are gilsonite and phenolic resins. Most of the blankets are made of cured rubber [4]. Bituminous enamels are made from coal tar pitches and petroleum bitumen. Natural asphalts, such as gilsonite, are sometimes used as well in combination with petroleum asphalts to enhance physical properties [5]. Addition of gilsonite to asphalt binder increases its viscosity and reduces its penetration. The result of such addition is a modified asphalt binder with higher hardness. Generally, gilsonite can be used in pavement construction in two ways: preliminary addition of gilsonite to the asphalt binder, or addition of gilsonite to aggregates during premixing cycle at batch plant. Research in the field of gilsonite application shows that gilsonite causes the performance improvement of asphalt binder in high temperatures, while in low temperatures it causes brittleness of the asphalt binder, and provides a suitable condition for low temperature cracking in pavement [1]. However using of natural bitumen in road making usually takes place with goal of standard products and low final cost, therefore if scale of using natural bitumen in the final product be more, product's final cost will be lower. One common method of bitumen produce is compound of natural bitumen with vacuum bottom of distillation column. Vacuum bottom (VB) is the heaviest cut of crude oil and obtained from the bottom of vacuum distillation tower in the refinery and it is as a raw material known in bitumen production. The composition of vacuum tower bottom residue is widely variable depend on crude oil consumption and the process of refining and will be large effect on the mechanical properties and structure of the bitumen produced. In some refineries that refining heavy crude oil and the temperature and pressure controlled in the vacuum tower it can be produced penetration grade bitumen for road construction directly. The penetration of vacuum tower bottom residue produced in Iran refineries is about 300 at 25 ° C and its viscosity close to 600 cS at 135 ° C, that is not suitable for direct usage in paving applications, except Abadan and Shiraz refineries that directly produce 60/70 bitumen grade. The most extensive process to convert the vacuum tower bottom residue to penetration grade bitumen is blowing hot air into the vacuum bottom [6].According to quotas and restrictions for the preparation

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of vacuum bottom in Iran; in this paper besides replacing Pyrolysis Fuel Oil for the vacuum bottom we study the compound effect with natural bitumen.

II. Materials

A. Natural Bitumen

When migration processes occur, mixtures of hydrocarbons, bitumens are formed in sedimentary or metasedimentary rocks or even on hydrothermal mineral deposits. These bitumens are first liquid, later, as influenced by different alteration processes (fluid migration, oxidation, thermal alteration) they can solidify. Their accumulations occur frequently in mineral or rock cracks and fissures, forming sometime vein type accumulations. We will use the name solid bitumen as general term for transformed accumulated solid bitumens in sedimentary and metamorphic rocks. We will reserve the term asphaltic-like solid bitumen(ALSB) to identify solid bitumens characterized by low carbonization degree (as gilsonites have).On the contrary, hard solid bitumen (HSB)designates solid bitumens with low H/C ratio (cata-impsonites, for example) [7]. Natural bitumen applied in this paper prepare form Avizheh Technology and Development of Middle East Company and it was used in powdered form that its physical properties has shown in Table 1.

TABLE 1PHYSICAL PROPERTY OF NATURAL BITUMEN

Test	Unit	Result
Ash content	%Wt.	0 ~ 5
Solubility in CS_2	%Wt.	89.5
Fixed carbon	%Wt.	29.7
Carbon Content	%Wt.	78.8
Hydrogen content	%Wt.	8.5
Sulfur content	%Wt.	4
Nitrogen content	%Wt.	1
Moisture content	%Wt.	1 ~ 3
Oxygen content	%Wt.	1.9
Penetration	dmm	0
Softening point	˚C	190 ~ 220

TABLE 2 PHYSICAL PROPERTY OF P.F.O

Test	Unit	Result
Sp.Gr. 60˚F/60˚F	--	1.1024
Viscosity @ 40˚C	cSt	5 ~ 15
Maximum water content	ppm	1000
Flash point	˚C	60
Pour point	˚C	-35 ~ -50

TABLE 3 RANGE OF CHANGES IN WEIGHT PERCENTAGE OF P.F.O AND NB

Component	Minimum Wt.%	Maximum Wt.%
Natural Bitumen	40	60
Pyrolysis Fuel Oil	40	60

B. Pyrolysis Fuel Oil

Pyrolysis fuel oil (P.F.O) is the byproduct of olefin production unit with liquid feed. The main route for producing light olefins, especially ethylene, is the steam cracking of hydrocarbons. The feedstock's for steam cracking units range from light paraffinic hydrocarbon gases to various petroleum fractions and residues. The cracking reactions are principally bond breaking and a substantial amount of energy is needed to drive the reaction toward olefin production. The simplest paraffin (alkane) and the most widely used feedstock for producing ethylene is ethane. As mentioned earlier, ethane is obtained from natural gas liquids. Cracking ethane can be visualized as a free radical dehydrogenation reaction. When liquid hydrocarbons such as naphtha fraction or gasoil are used to produce olefins, many other reactions occur. The main reaction, the cracking reaction, occurs by a free radical and beta scission of the C-C bonds [8]. If every tack be heavier, then more pyrolysis fuel is produced. The applied P.F.O in this paper has been prepared from Iran Amirkabir Petrochemical Company that its physical properties have been shown in table 2. For studding the chemical compound of P.F.O, F.T.I.R test was performed on the sample whose result can be seen in figure 1.

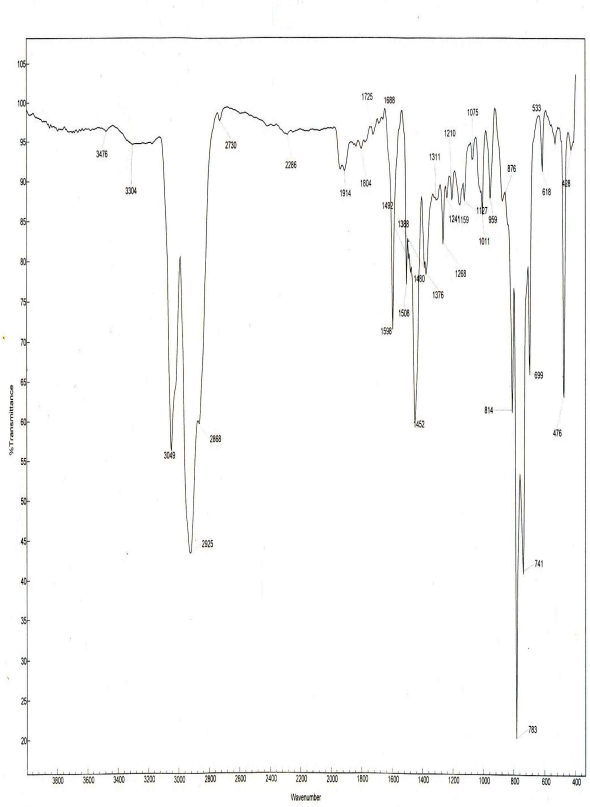


Figure 1 P.F.O, F.T.I.R Test Result

TABLE 4. RESULT OF SAMPLE PROPERTIES

Sample	NB	Penetration at 25°C	Softening point	Ductility at 25°C	PI
	(Wt. %)	(0.1 mm)	(°C)	(cm)	
Blend 1	40	152	64.4	6.2	5.6
Blend 2	45	56	94.9	5.8	6.4
Blend 3	50	28	109.6	5.5	6.1
Blend 4	55	15	118.1	5	5.5
Blend 5	60	7	123.8	4.6	4.7

TABLE 5 STANDARD PROPERTIES RANGE

Property / Bitumen Type	Penetration at 25°C (0.1 mm)	Softening point (°C)
85/25	20~30	80~90
85/40	35~45	80~90
95/25	20~30	90~100
95/35	30~40	90~100
100/40	35~45	95~105
105/35	30~40	100~110
110/30	25~35	105~115
115/15	10~20	110~120
Test methods	EN 1426	EN 1427

III. Experimental

First, weight percentage change rate of P.F.O and NB for mixing by using a linear combination of primary properties of raw material and oxide bitumen R 95/25 were estimated which is shown in table 3. To mix the material, first P.F.O should be heat to the temperature of 80 ° C, and NB is added to it gradually. Whole the time for each sample is 3 hours and the temperature of the mixer was in created by the coil existed in it from 80 to 220 ° C gradually. Speed of the mixer was 2500 round per minute, and then the mixture is transferred to another container by valve. Schematic of mixer is shown in figure 2. Later, penetration test, softening point and ductility test were done on the samples.

IV. Mathematical Calculation

All bitumen's display thermoplastic properties, i.e., they become softer when heated and harden when cooled. If the logarithm of penetration, P, is plotted against temperature, T, a straight line is obtained such that log P=A.T+K. Where A is the temperature susceptibility of the penetration and K is a constant. Pfeiffer and van doormaal developed an equation for the temperature susceptibility that assumes a volume of about zero for road bitumens. For this reason they defined the penetration index (PI) as:

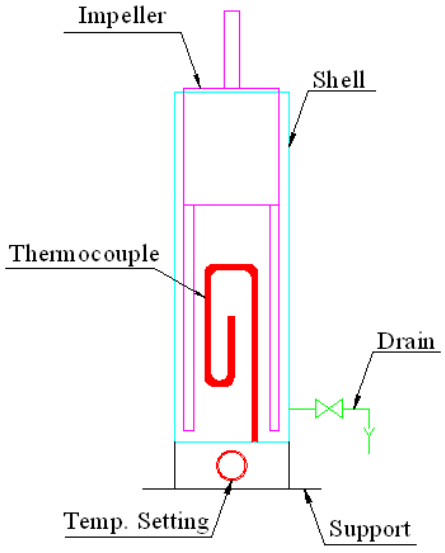


Fig. 2. Schematic of Mixer

$$PI = \frac{20(1-25A)}{1+50A}$$

$$A = \frac{\log Penetration\ @T_1 - \log 800}{T_1 - T_{SP}}$$

T_1 is the penetration test temperature and T_{SP} is the ASTM softening point.

The value of PI ranges from around -3 for highly temperature susceptible bitumens to around +7 for highly blown low temperature susceptible bitumens [9].

V. Result

Because Results of the tests on the samples have been shown in table 4 and properties of the oxidize bitumens in accordance with BS EN13304: 2009 standard has been shown in table 5. It is clear that sample blend 3 which includes 50% natural bitumen , 50% P.F.O is in accordance with the properties of oxidize bitumen 110/30. Also, sample blend 4 which includes 55% natural bitumen and 45% P.F.O, is located in the accepting range of oxidize bitumen 115/15.

In BS EN13304: 2009 standard scope of acceptance for ductility test is not presented but in standard ASTM D 312 , result of ductility test, is determined at least 1.5 cm for the same bitumens and as it is clear in the table 4 , all produced samples have ductility more than the determined quantity. Adding the natural bitumen to the mixture causes increasing in the softening point and decreasing in penetration of the bitumen. These changes have been shown in figure 3.

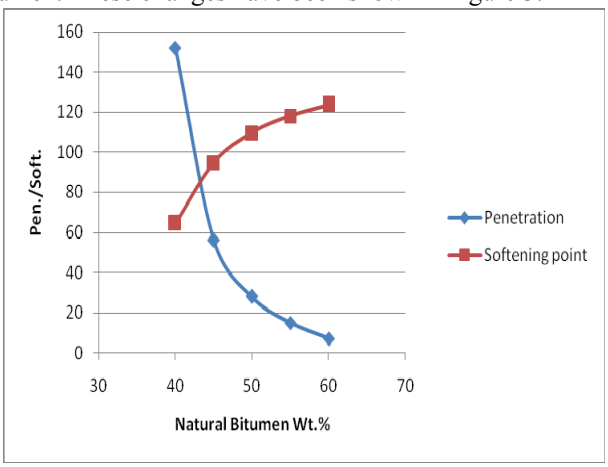
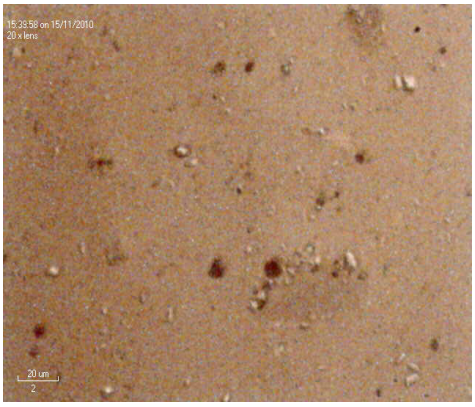
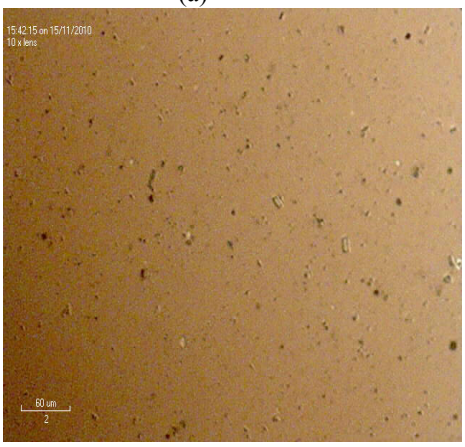


Fig. 3. Penetration and Softening Point Changes with Natural Bitumen



(a)



(b)

Fig. 4. Morphology of Sample 3. a) Scale 60 micrometer. b) Scale 20 micrometer

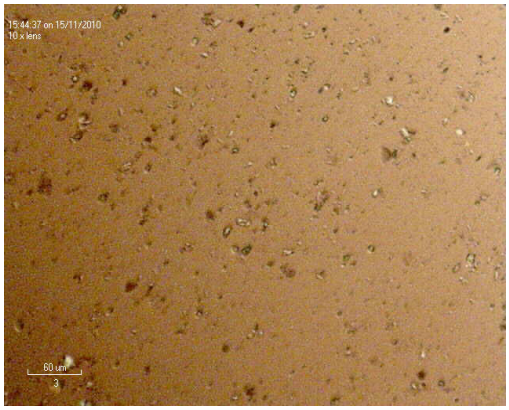
We can see in the table 4 that penetration index of whole samples is in the acceptance area (-3<pi<+7). It should be noted that this value for the oxide bitumen (blown bitumen) that is higher that the value obtained from penetration grade bitumen because of the high softening point and low penetration of bitumen and show the low temperature susceptible of them. Morphology of sample 3 and 4 shows in figure 4 and figure 5 respectively and shows that the natural bitumen is well distributed in P.F.O and has produced a homogeneous mixture.

It seems that change in the processing conditions (e.g. Increasing heat or time of mixing the samples) can cause the more solubility of the natural bitumen. Impurities particles are seen in the figures, which show the ashes have a mineral source and it is not solved in to toluene and the condition BS EN 1304 standard should use the natural bitumen whose ashes has separated from it. To recover bitumen, the processes of aqueous extraction are used: a ‘‘dying out” classical process with treatment by steam and hot water with caustic addition (conditioning) in rotating drums [10].

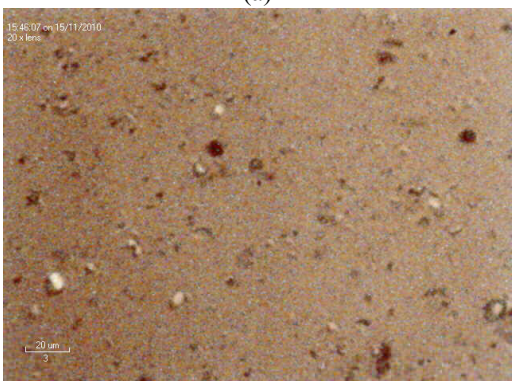
VI. Discussion and Conclusions

Producing the new material which is a combination from

The natural bitumen and the vacuum distillation tower residue are widely used in corrosion protective coatings and water proof coating. Regarding to the limited level of producing vacuum bottom in the refineries displacing it with the material of P.F.O was studied in this paper. P.F.O in its cost equals to vacuum bottom so from the economical point of view, this displacement won’t result in increasing the cost of the final product. Results of the tests performed on the different samples as shown in figure 6 indicated that on expanded range of oxide bitumen can be produced from this combination. For instance, two kind of oxide bitumen grade 110/30, 115/15 were produced in accordance with the BS EN 1304 standard specification. A significant note is the existence of ashes in the natural bitumen which is seen unsolvable in P.F.O and should use ash free natural bitumen.



(a)



(b)

Fig. 5. Morphology of Sample 4. a) Scale 60 micrometer. b) Scale 20 micrometer

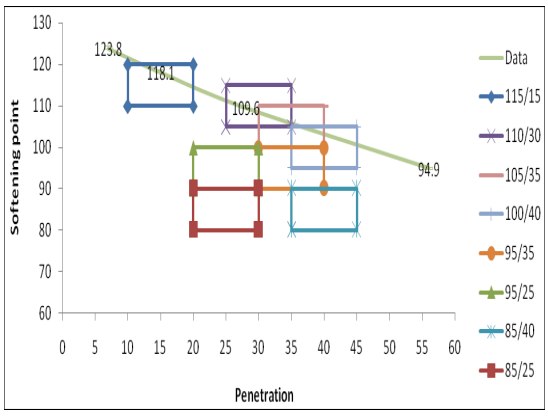


Fig. 6. Samples Properties Change in Standard Properties Range

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REFERENCES

[1] M. Ameri, A. Mansourian, S. S.Ashani, G. Yadollahi, "Technical study on the Iranian Gilsonite as an additive for modification of asphalt binders used in pavement construction", *Construction and Building Materials,* vol. 25(3), 2011, p- 1379-1387.

[2] E.V. Oort," On the physical and chemical stability of shales", *Journal of Petroleum Science and Engineering*, vol. 38, 2003, p- 213– 235.

[3] R.S. Dungan, J.B. Reeves," Pyrolysis of carbonaceous foundry sand additives: Seacoal and gilsonite", *Thermochimica Acta,* vol. 460, 2007, pp- 60–66.

[4] L.E.K. Achenie, M. Sinha," The design of blanket wash solvents with environmental Considerations", *Advances in Environmental Research,* vol. 8, 2003, p- 213–227.

[5] S.W. Guan," Corrosion protection by coatings for water and wastewater pipelines", *AUCSC Water and Wastewater Program*, West Virginia University, 2001.

[6] S.B. Mortazavi, Y. Rasoulzadeh, A.A. Yousefi, A. Khavanin," Properties of Modified Bitumen Obtained from Vacuum Bottom by Adding Recycled Waste Polymers and Natural Bitumen", *Iranian Polymer Journal,* vol.19 (3), 2010, p-197-205.

[7] J. Jehlic˘ka, O. Urban, J. Pokorny," Raman spectroscopy of carbon and solid bitumens in sedimentary and metamorphic rocks", *Spectrochimica Acta Part A,* vol. 59, 2003,p-2341_2352.

[8] S. Matar, L.F. Hatch," Chemistry of Petrochemical Processes", Gulf Publishing Company, Second edition, 2000

[9] J. Read, D. Whiteoak," The Shell Bitumen Handbook", *Thomas Telford Publishing, Fifth edition*, 2003.

O.V. Abramov ,V.O.Abramov,S.K. Myasnikov,M.S.Mullakaev," Extraction of bitumen, crude oil and its products from tar sand and contaminated sandy soil under effect of ultrasound", *Ultrasonics Sonochemistry*,vol.16,2009,pp-408–416.

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