Heavy product from co-processing of FCC slurry and coal as bitumen modifier

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Introduction

Co-processing of coal and petroleum resid has been developed to produce liquid fuels, and has gained significant advancements during past several decades. In this work the co-processing process is adopted to produce a bitumen modifier under mild conditions. The modifier is the heavy portion of the co-processing products including un-reacted materials and ash in the coal. Oil is a byproduct. Market price of similar natural occurring modifier is about $500-$750/t in China, which is much higher than the prices of oil and road paving asphalt.

Bitumen on road experiences a wide range of static and dynamic stress at varying temperature under different environmental conditions. The lifetime of the road surface is limited due to aging of bitumen in asphalt concrete mix. Addition of non-vulcanized nature and synthetic polymers to improve the properties of paving asphalt are well known and widely used (1, 2). Reclaimed rubber, pulverized waste tire and special naturally occurring asphalt (such as Trinidad lake asphalt) are also used as additives (3, 4). Addition of these materials improves durability of asphalt surface, adhesion of bitumen to aggregate, deformation resistant at great load and freeze resistance.

Due to super road performance (4), compared to other additives, Trinidad lake asphalt (TLA) has been used in bitumen modification worldwide.

In this study slurry, from fluidized catalytic cracking (FCC) unit, and coal is co-processed. The heavy product, named MCSC (modifier from co-processing slurry and coal), is tested for possible usage on bitumen modification. Modification ability and physical and chemical properties of MCSC are presented and compared with TLA.

Experimental

The FCC slurry (FCCS), from Shijiazhuang Petroleum Refinery of China, and a Chinese bituminous coal (YZ), were used to make the modifier, MCSC. The properties of FCCS and the coal are listed in Tables 1 and 2. The base bitumen used to test the modification ability of the modifier was Binzhou 90# (AH 90 in Chinese standard specification) with a penetration value of 95. The base asphalt was mixed mechanically with the modifier.

The co-processing was carried out in a 50-liter autoclave with a magnetic stirrer under hydrogen or nitrogen pressures of 8-14 MPa at temperatures of 400-450°C for 1-3 hours. The coal was pulverized to <100 mesh and impregnated with a Fe (1 wt%) or a Mo (0.04-0.4 wt%) catalyst precursor (5). The ratios of FCCS to coal were 1:1 and 2:1. The autoclave was directly connected to a 40-liter vacuum distillation unit. After the co-processing, the mixture was discharged into the distillation unit and the oils were distilled out at 330°C and 0.01MPa. The residual materials were MCSC and collected from the bottom of the distillation column. Typically the MCSC yield ranged from 65-80% and oil yield 10-25% (boiling point ranged from 100-450°C).

The Technical Specifications of JTJ 036-98 for Construction of Highway Modified asphalt Pavement, and standard test methods JTJ 052-2000 for Bitumen and Bituminous Mixtures of Highway Engineering by Ministry of Communications of The People's Republic of China, were used.

Table 1. The Properties of the FCCS Used, wt% as[1]

Elemental composition				
C	H	N	S	H/C, atomic
88.97	8.12	0.48	1.35	1.1
Group composition				
Saturates	Aromatics	Resins	Asphaltenes	
6.7	65.7	18.7	8.9	

1: "as" denotes "as received"

Table 2. The Properties of the Coal, wt% as[1]

Proximate analysis				
Moisture	Ash	Volatile Matter		
1.50	4.17	42.86		
Ultimate analysis				
C	H	N	S	H/C, atomic
75.92	5.01	1.32	2.02	0.79

1: "as" denotes "as received"

Results and Discussion

The properties of a typical MCSC and TLA are compared in Table 3. There is no significant difference in physical properties listed in the first five lines. The main differences are in the last two lines, which reveal the higher aromaticity of MCSC than TLA, the lower hydrogen content and the higher aromatic hydrogen distribution in MCSC. The high contents of organic residue and pre-asphaltene are significant factors, which differentiate MCSC from TLA.

Comparisons of modification abilities of MCSC and TLA are given in Tables 4 and 5. The mixing ratio of the modifier to the base bitumen is 20:80. The notation 90#/MCSC refers to a modified Binzhou 90# by MCSC, 90#/TLA refers to a modified Binzhou 90# by TLA. From Table 4 it can be seen that both MCSC and TLA alter the properties of the base bitumen, increasing the softening point by about 4-8°C and decreasing the penetration value by about 51-54 points. This indicates that the modified bitumen becomes harder than the base bitumen. Usually, this change may result in loss of viscous-elasticity to some extent. But the data show that the viscous-elasticity of the modified bitumen samples is still very good as demonstrated by the high ductility values at 15°C and 25°C. The Retained penetration (the ratio of penetration value after and before TFOT, thin-film oven test, which represents the ability on resisting the fast aging) of both modified samples are also higher, suggesting higher high-temperature stability. The ductility of 101 mm for 90#/MCSC at 15°C suggests higher low-temperature stability of the sample. All these data suggest that the properties of 90#/MCSC are significantly better than that of 90#/TLA.

Table 5 compares dynamic stabilities between 90#/MCSC and 90#/TLA samples determined in the rutting test. Rutting is generated at a wheel path of carriageway in the cases of warmer climate

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conditions, heavily trafficked roads, approaches to intersections and climbing lanes. Dynamic stability of hot mix asphalt (HMA) against rutting is an important property of asphalt mixture in wearing course. It represents the ability to resist shoving rutting under traffic and elevated temperature. For hot mix modified bitumen mixture this value should be greater than 800-3000 wheel passes/mm depending on the climate encountered. It is clear that the dynamic stabilities of both samples are similar and meet the highest required value.

Table 3. The Properties of Typical MCSC and TLA

Items	MCSC	TLA
Specific gravity	1.15	1.39-1.44
Softening point (R&B), ^{o}C	102	93-99
Penetration at 25°C, 100g, 5s	8	0-4
Weight loss after thin-film oven test, %	<1	<2
Solubility in trichloroethylene, %	53	52-55
Inorganic residue, %	3	35-39
Organic residue, %	20	8
Preasphaltene, %	33	0.73
THF solubles, %	75	56
H/C, atomic	0.8	1.4
Aromatic/aliphatic hydrogen ratio by FTIR	7.4	0

Table 4. The Properties of Binzhou 90# and Two Modified Bitumen

Items	90#	90# /MCSC	90# /TLA
Softening Point (B&R), ℃	44.2	48.0	51.7
Penetration at 25℃, 100g, 5s	95	44	41
Ductility at 25 ℃, 5cm/min, cm	>150	>150	>150
Ductility at 15 ℃, 5cm/min, cm	>150	101	52
Flash point, ℃	>240	>240	>240
TFOT			
Softening Point (B&R), ℃	48.7	53.6	56.1
Penetration at 25℃, 100g, 5s	57	36	26
Retained penetration after thin-film oven test, %	60	82	63
Ductility at 25℃, 5cm/min, cm after thin-film oven test	150	144	100
Weight lost, ％	0.100	0.255	0.418

Table 5. The Results of the Rutting Test

Sample	90#/MCSC	90#/TLA
Dynamic stability, wheel passes/mm (60°C, 0.7 MPa)	2000-3500	3100

Further comparison on the properties of 90#/MCSC and 90#/TLA samples with ASTM standard specification, D5710-95, designated to Trinidad lake modified asphalt, showed that both modified samples meet the specifications.

It was also found that the properties of the modifier are related on the co-processing conditions used, such as temperature, atmosphere, pressure, type of catalyst, catalyst loading, FCCS to coal ratio and reaction time. Two or more modifiers can also be blended to obtain the desired properties. The properties of the modifier can be manipulated by controlling the co-processing conditions.

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Conclusions

A heavy product (MCSC) produced from co-processing of a fluidized catalytic cracking slurry with a coal was used as bitumen modifier in asphalt concrete mix. The modification capability of MCSC is similar to that of a commercial bitumen modifier, Trinidad lake asphalt (TLA), and meets ASTM standard specification of D5710-95. Comparing to TLA, MCSC contains more aromatic, condensed, small molecular weight component.

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